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Surface Induced Crystallization in Fiber Reinforced Semicrystalline
Thermoplastics Composites

by

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This paper reviews the parameters influencing the appearance of a transcrystalline zone and the experimental techniques which have been used in the study of transcrystallization. A significant example is given for each characterization technique. The influence of transcrystallinity on the mechanical properties of the composite is then examined. Lastly, a theoretical approach based on the theory of heterogeneous nucleation and on the induction time is presented, which allows to control the extent of the transcrystalline morphology. Little has been published on the mechanical aspect of transcrystallinity but this is an important aspect because this will ultimately determine if it is desireable to induce transcrystallization in semicrystalline thermoplastic composites. Although the main application of transcrystallization seems to be in fiber reinforced composites, results of studies with films as a substrate are directly applicable to fiber reinforced composites and have also been included in this chapter.

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OUTLINE

8.1 Introduction

In recent years, there has been a renewed interest for fiber reinforced thermoplastic composites. The influence of the fiber/matrix interface and of the matrix interphase on the mechanical properties of such composites is now well recognized and the concept of interface/interphase tailoring has emerged. In this respect, semicrystalline thermoplastic composites are of particular interest. Unlike thermoset composites, surface induced crystallization may result in a particular morphology at the interface, depending upon certain thermodynamic and/or physicochemical conditions. Surface induced crystallization, also refereed to as transcrystallization, arises when the nucleation density at the fiber surface is so high that the lateral development of the spherulites is impeded and growth can only proceed perpendicular to the fiber direction. Thus, a columnar growth region is produced which extends to the bulk matrix where spherulitic morphology is present. Fig. 8.1 shows a model for the formation of a transcrystalline zone, along with a typical example. Such a particular morphology is expected to have an influence on the adhesion at the interface by increased nucleation density and on the mechanical properties of the interphase due to preferential orientation of the lamellae. Transcrystallization has been observed for a variety of substrates and crystallizing conditions. It has also been reported in cast metals (Barrett, 1952). With high fiber content or under special conditions (see Sec. 8.6.2) it is possible to develop an entirely transcrystalline sample. In this case, the notions of an "interphase" and a bulk matrix disappear and the knowledge of the properties of the transcrystalline zone becomes essential.

Although the first report on transcrystallization dates back to 1952 (Jenckel et al., 1952), it remains a poorly understood and highly controversial

phenomenon. In particular, there is little or no mention of transcrystallization in well recognized polymer morphology handbooks (Geil, 1963; Sharples, 1966; Bassett, 1981) and, to the authors knowledge, no other review article has been published on the subject. This lack of information is mostly due to the following situation. In most of the earlier reports, transcrystallization was not the main focus of the study and was reported as a side consequence of the substrate/polymer pair or the thermodynamic conditions chosen. However, with the development of thermoplastic composites, a better knowledge of the influence of the transcrystalline zone on the composite properties has become necessary. Several problems make this study difficult.

First, transcrystallization is often observed as the result of the combined effect of several different parameters. It is therefore difficult to identify the most important contribution. Moreover, there is not always unanimity among authors concerning the influence of a each parameter on transcrystallinity. All too often this is due to the fact that the investigator wants to reduce the appearance of transcrystallization to one essential parameter whereas it is more likely that a combination of parameters is involved. This explains many of the seemingly contradictory reports found in the literature. However, most of the parameters influencing the appearance of a transcrystalline zone have been identified by now.

Second, most of the published work has been qualitative in nature and little has been done in the direction of morphology control. Very few attempts have been made to quantitatively characterize the nucleating ability of a given substrate toward a particular polymer. As it will be shown later, this is mostly due to a practical limitation of the theory of heterogeneous nucleation. A quantitative approach is needed if one wants to compare different fiber/polymer

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systems exhibiting transcrystallization or if the extent of the transcrystalline zone is to be controlled.

Also, it is very difficult to recognize and separate the contribution of transcrystallinity to the adhesion at the fiber/matrix interface and to the mechanical properties of the interphase region. This last point is of great importance because researchers have been arguing on the real role of transcrystallinity based on the difficulty to prove unambiguously any improvement in mechanical properties.

This chapter reviews the parameters influencing the appearance of a transcrystalline zone and the experimental techniques which have been used in the study of transcrystallization. A significant example is given for each characterization technique. The influence of transcrystallinity on the mechanical properties of the composite is then examined. Lastly, a theoretical approach based on the theory of heterogeneous nucleation and on the induction time is presented, which allows to control the extent of the transcrystalline morphology. Little has been published on the mechanical aspect of transcrystallinity but this is an important aspect because this will ultimately determine if it is desirable to induce transcrystallization in semicrystalline thermoplastic composites. Although the main application of transcrystallization seems to be in fiber reinforced composites, results of studies with films as a substrate are directly applicable to fiber reinforced composites and have also been included in this chapter.

In this chapter, the terms "surface induced crystallization", "transcrystallization" and "epitaxial crystallization" have been used. Although the three terms refer to the same basic phenomenon, the terms do become increasingly restrictive. "Surface induced crystallization" is the most general term whereas "transcrystallization" is more indicative of the visual phenomenon

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because growth proceeds transverse to the fiber direction. However "transcrystallization" only implies that the b axis of the polymer is perpendicular to the fiber. "Epitaxial crystallization" is the most restrictive because the orientation of the b and c axis are fixed. Whenever possible, the occurrence of melt epitaxy should be recognized because the degree of lamellar orientation at the surface is higher than for regular transcrystallization and may influence the mechanical properties of the interphase.

8.2 Classification of Substrate Activity

8.2.1 Empirical Approach

Figure 8.1 is an example of a well developed surface induced morphology where large transcrystals (of the order of 20 µm) can be seen. However, depending on the nature of the polymer/substrate pair and on the crystallization conditions, intermediate morphologies can be observed. In an effort to rationalize the study of surface induced crystallization, Chatterjee and Price (1975a) first introduced a classification of substrates with respect to their nucleating ability. Based on optical microscopy observations of over 43 polymer/substrate pairs, they distinguished three main types of substrates:

Type 1: Very active substrates: nucleation is favored at the substrate surface compared to the bulk polymer. Transcrystalline morphology is observed.

Type 2: Moderately active substrates: depending on the nucleation density, a mixed transcrystalline-spherulitic morphology is observed. As the nucleation density decreases, the surface morphology becomes mostly spherulitic.

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Type 3: Inactive substrates: bulk nucleation is favored over surface induced nucleation and little or no spherulites are seen at the interface.

As a first step, this qualitative classification is very useful for comparing the activity of different substrates toward a particular polymer. Chatterjee and Price (1975a) have also stressed that surface induced crystallization is a competitive process. If the bulk nucleation density is very high, there is little chance to develop a large transcrystalline zone because the transcrystals will immediately impinge on bulk spherulites even if surface nucleation density is high. This remark calls for two further observations. First, transcrystallization is a nucleation controlled phenomenon. Therefore it seems essential to study the nucleation step because once nucleation has occurred, growth in the matrix and on the fiber proceeds in exactly the same way. In particular, the extent of the transcrystalline zone is not an indication on the nucleating ability of the fiber toward the melt. This is an important point because much of the literature has linked the substrate propensity to induce transcrystallization to the extent of the transcrystalline zone. A large transcrystalline zone can indicate a high surface activity and/or a weak bulk nucleation. Second, any quantitative study must take into account the bulk heterogeneous nucleation in the matrix because this will determine the extent to which the transcrystalline growth front can proceed in the matrix.

This qualitative approach, however, does not take into account the temperature dependency of these morphologies. It is well-known that nucleation density is highly dependent on the degree of supercooling. Because the surface nucleation density and the bulk nucleation density exhibit a different temperature dependency, their relative magnitude and hence the resultant morphology will vary with temperature. In the following section, a more quantitative approach is

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presented based on the value of the free energy difference function as it appears in the theory of heterogeneous crystallization.

8.2.2 Theoretical Approach

The previous discussion has demonstrated the need for a more quantitative approach to surface induced crystallization. A theoretical approach to transcrystallization is needed for several reasons. It is desirable to be able to compare the nucleating ability of different polymer/substrate pairs independently from temperature and on a more objective basis than the current evaluation from optical micrographs. One would also like to explain the observed or expected effects of such parameters as crystallization temperature, cooling rate or surface energy. Last, one would like to be able to use the theory as a guideline to control the extent of the transcrystalline morphology.

In a theoretical approach, it is desirable to determine the amount of energy necessary to create a stable nucleus at the fiber surface and how this energy is affected by the various parameters mentioned above. In the classical nucleation theory (Wunderlich, 1976), the overall free enthalpy of crystallization is written as:

$$\Delta G = \Delta G_C + \sum_i \sigma_i A_i \qquad (8.1)$$

where ΔG_C represents the bulk free enthalpy change (Gibbs free energy) involved in the melt-crystal phase transition and is related to the volume of growing crystal. ΔG_C is negative and is the driving force in the crystallization process. The opposing force (positive contribution to the free enthalpy of crystallization) arises from the creation of new surfaces A_i having a specific

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surface free energy σ_i. Initially, the driving force is not strong enough to overcome the amount of energy necessary to create new surfaces and ΔG is positive. However, because the volume to surface area ratio increases as new crystallizable elements are added to the nucleus, ΔG exhibits a maximum (critical free enthalpy ΔG^*) and eventually becomes negative. The nucleus then becomes stable (Fig. 8.2). When no impurities are present in the melt to initiate nucleation, the nucleation is termed homogeneous. However in most cases, there are always some kind of foreign surfaces provided by heterogeneities (catalyst residues, dust particles, ...) or by remnant order in the melt (partially molten spherulites, local chain alignment due to flow conditions, ...). A foreign surface reduces the critical free enthalpy of formation of a nucleus because the energy required to create an interface between the foreign surface and the polymer crystal is often significantly less than that of the corresponding polymer crystal surface. In this case the nucleation is termed heterogeneous. For a large substrate (film or fiber), a high nucleation density will result in a transcrystalline morphology.

Compared to the dimensions of a heterogeneous nucleus (a few tens of nanometers) a fiber or a film can be treated as a flat surface. This model is very convenient because it has been used in most of the published studies (Chatterjee and Price, 1975c; Koutsky et al.,1967) dealing with heterogeneous nucleation. This enables comparison with the data found in the literature. Fig. 8.3 presents the parameters defining the heterogeneous nucleus. a, b and l represent the dimensions of the nucleus. σ is the side surface free energy and σ_e is that for the fold surface (high energy surface). A marked difference between heterogeneous and homogeneous nucleation is the introduction of $\Delta\sigma$, the interfacial free energy difference function. $\Delta\sigma$ is related to the creation of a new

(al) top surface. A better understanding of the nature of $\Delta\sigma$ is achieved when it is related to its three basic components (Cherry, 1981) :

$$\Delta\sigma = \gamma_{cs} + \gamma_{cm} - \gamma_{ms} \tag{8.2}$$

where γ_{cs} is the crystal-substrate interfacial free energy, γ_{cm} is the crystal-melt surface free energy ($\gamma_{cm} = \sigma$ as defined earlier) and γ_{ms} is the melt-substrate interfacial free energy. For hydrocarbons, where dispersion forces are predominant (no polar interactions), Fowkes (1964) further expres. d the interfacial free energy, γ_{ab}, as:

$$\gamma_{ab} = (\gamma_a^{1/2} - \gamma_b^{1/2})^2 \tag{8.3}$$

where γ_a and γ_b represent the dispersion components of the surface tension for phase a and b. In theory, $\Delta\sigma$ can be therefore expressed as a function of the surface tension properties of the substrate, polymer crystal and polymer melt. Because the surface (al) is the only one to see the substrate, $\Delta\sigma$ is a convenient way to define the nucleating ability of a substrate toward a polymer melt. A lower value of $\Delta\sigma$ reduces the value of ΔG^* and indicates a more favorable nucleation process. The limiting value of $\Delta\sigma$, $\Delta\sigma = 0$, is reached when secondary nucleation occurs, i.e when there is no difference between the substrate and the polymer crystal. This is the basic process by which growth occurs in polymers. In this case, $\gamma_{cs} = 0$, $\gamma_{cm}=\gamma_{ms}$ and thus $\Delta\sigma = 0$ (Eq. (8.2)). However $\Delta\sigma$ should not be considered alone because, unless special precautions are taken, the transcrystallization process will have to compete with bulk heterogeneous nucleation in the matrix.

In the following section, $\Delta\sigma$ designates the interfacial free energy difference function in a substrate/crystallite system whereas $\Delta\sigma'$ is that of a

heterogeneities/crystallite in the melt system. Clearly the relative magnitude of $\Delta\sigma$ and $\Delta\sigma'$ influences the whole nucleation in the composite sample and its final morphology. In an effort to rationalize the classification of substrate activity first introduced by Chatterjee and Price (1975a), Ishida and Bussi (1990a) defined the advantage, A, for a polymer to crystallize at the substrate surface rather than in the bulk as the ratio of $\Delta\sigma'$ and $\Delta\sigma$:

$$A = \Delta\sigma' / \Delta\sigma \qquad (8.4)$$

The following three situation are encountered (Tab. 8.1):

$A \approx 0$ $(\Delta\sigma \gg \Delta\sigma')$	Inactive substrate. The polymer melt ignores the presence of the fiber and there is no nucleation at the fiber/film surface.
$0 < A < 1$	Moderately active substrate. Spherulitic surface morphology is observed. Transcrystallinity becomes more probable as A approaches 1.
$A \geq 1$	Very active substrate. Nucleation is heavily favored at the fiber surface. Transcrystallinity is observed.

In order to calculate A, one needs to estimate $\Delta\sigma$ and $\Delta\sigma'$. They may be practically obtained through a combined growth and nucleation rate experiment. According to the theory of polymer nucleation (Wunderlich,1976) the rate of heterogeneous nucleation is given by:

$$I = I_0 \cdot \exp\left(-\frac{\Delta\varphi}{kT}\right) \cdot \exp\left(-\frac{\Delta G^*}{kT}\right) \qquad (8.5)$$

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where I_0 is a constant nucleation rate, $\Delta\varphi$ is the activation energy for a molecule to cross the phase boundary and ΔG^* is the critical excess free energy due to the creation of a nucleus. k is Boltzmann's constant and T is the crystallization temperature. ΔG^* can be further expressed as:

$$\Delta G^* = \frac{16\,\sigma\sigma_e\Delta\sigma}{\Delta g_f^{\,2}}$$

(8.6)

where σ, σ_e and $\Delta\sigma$ have been defined previously. Δg_f is the bulk free energy of fusion per unit volume of crystal. In general, Δg_f can be expressed as (Hoffman et al., 1976):

$$\Delta g_f = \frac{\Delta h_f\,\Delta T}{T_m^0\,f}$$

(8.7)

where Δh_f is the heat of fusion per unit volume of crystal at the equilibrium melting point T_m^0 and ΔT is the degree of supercooling. Δg_f has to be corrected by a factor f since Δh_f varies with the crystallization temperature:

$$f = \frac{2T}{(T_m^0 + T)}$$

(8.8)

At low supercooling, f has little influence, but it must be taken into account as the crystallization temperature decreases (see for example Fig. 8.20). The heterogeneous nucleation rate can then be rewritten as:

$$I = I_0 \cdot \exp\left(-\frac{\Delta\varphi}{kT}\right) \cdot \exp\left(-\frac{16\,\sigma\sigma_e\Delta\sigma\,T_m^{0\,2}}{k\,T\,\Delta T^2\Delta h_f^{\,2}f^2}\right)$$

(8.9)

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Once heterogeneous nucleation has occurred, growth will proceed by adsorption and crystallization of polymer molecules at the initial nucleus surface. This process is also refereed to as secondary nucleation, as compared to primary nucleation starting at the substrate surface. Intuitively, one can feel that $\Delta\sigma$ does not play any role in this case since no new (al) surface is created. Two processes or regimes of growth can be distinguished (Hoffman et al., 1976) (Fig. 8.4). In regime I, the completion of a new layer is rapid compared to the rate of nucleation, whereas, in regime II multiple nucleation occurs at the substrate surface before a layer is completed. These different processes are reflected in the expression of ΔG^* and the net growth rate is given by:

$$g = g_0 \cdot \exp\left(-\frac{\Delta\varphi}{kT}\right) \cdot \exp\left(-\frac{\beta\, b_0\, \sigma\sigma_e\, T_m^o}{kT\, \Delta T\, \Delta h_f f}\right) \tag{8.10}$$

where g_0 is a constant growth rate and b_0 is the thickness of a new layer. b_0 can be related to the Miller's indices of the polymer unit cell. β is a constant characterizing the regime of growth: for regime I, $\beta=4$ whereas for regime II, $\beta=2$. Since regime II requires a higher nucleation rate, it is observed at a higher degree of supercooling.

It should be mentioned here that the activation energy, $\Delta\varphi$, has a much smaller influence on the nucleation rate than the term due to the free energy difference, $\Delta\sigma$. This is true particularly at low supercooling where the mobility of the polymer chains is still high. In the treatment of data, a WLF (William-Landel-Ferry) type of temperature dependency is often assumed (Hoffman et al., 1976).

By looking at Eq. (8.9) and Eq. (8.10), one can readily see that the nucleation rate is a function of $1/T(\Delta T f)^2$, whereas the growth rate depends on

$1/T(\Delta Tf)$. A plot of $\ln I + \Delta\varphi/kT$ versus $1/T(\Delta Tf)^2$ should yield a straight line whose slope, K_i, is proportional to $\sigma\sigma_e\Delta\sigma$. Similarly a plot of $\ln g + \Delta\varphi/kT$ versus $1/T(\Delta Tf)$ should yield a straight line whose slope, K_g, is proportional to $\sigma\sigma_e$. A combined nucleation and growth experiment thus yields estimates of $\sigma\sigma_e\Delta\sigma$ and $\sigma\sigma_e$ from which $\Delta\sigma$ is obtained. Such an approach has been taken by Chatterjee and Price (1975c) to characterize the nucleating efficiency of isotactic polystyrene and isotactic polypropylene in the crystallization of polybutene. Koutsky et al. (1967) took a similar approach but used non-isothermal data to study the heterogeneous nucleation of polyethylene on cleaved surfaces of alkali halides.

However attractive, the approach described above has a very serious limitation when applied to the study of transcrystallization. In the case of heterogeneous crystallization in the polymer melt, the rate of appearance of individual spherulites can be recorded without difficulty. This observation, coupled with growth rate measurements, enables us to determine $\Delta\sigma'$. But in the study of surface induced crystallization (determination of $\Delta\sigma$), this approach is applicable only if the substrate shows a moderate activity. For a better nucleating substrate, the crowding of spherulites at the fiber surface makes any count nearly impossible. In the limiting case of transcrystallinity the nucleation density cannot be measured. Consequently, the theory is restricted at this stage to polymer/substrate pair with a certain window of $\Delta\sigma$, i.e when A is much smaller than 1. In particular, this explains why, in their study of 43 polymer/substrate pairs, Chatterjee and Price (1975c) had to select two adequate systems which showed only a partial transcrystalline character. Recently, however, Ishida and Bussi (1990a,b) have proposed a different approach applicable to truly transcrystalline systems. This approach, based on induction time, is presented in Sec. 8.6.

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8.3 Parameters Influencing the Appearance of a Transcrystalline Zone

8.3.1 Thermodynamic Parameters

In most of the early work on transcrystallization, the effect of various cooling rates was investigated, often with mixed results. Barriault and Gronholz (1955) found that for Nylon 66 in contact with various media (air, oil, water and silicone), the transcrystalline structure is not present only upon very rapid quenching. In the original report on transcrystallization, Jenckel et al. (1952) quenched polyamide in oil and water from about 20°C above the melting point (i.e around 240°C) to various temperatures and showed that eventually, transcrystallization disappears when the quenching temperature is reduced to 40°C (Fig. 8.5). A similar observation was made by Tung and Dynes (1987) for carbon fiber reinforced poly(ether-ether-ketone) composites quenched at various rates (from 1.5°C/min to 2500°C/min). In contrast, Fitchmun and Newman (1970) found that the morphology was independent of the cooling rate and noted the importance of the presence of a temperature gradient. By rapidly cooling a polymer from a temperature above the melting point, a transient temperature gradient develops through the sample which favors a higher nucleation rate at the surface than in the bulk. For large gradients, the likelihood of a transcrystalline layer increases, independently of the nature of the substrate. The effect of a temperature gradient is also reflected in the size distribution of the bulk spherulites and in the extent of the transcrystalline zone, e.g. a fast cooling rate producing a thinner transcrystalline layer. This is often observed in

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compression molded polymer films (polyethylene, polyamide, polypropylene with aluminum and Mylar: Fitchmun and Newman (1970); poly(vinylidene fluoride) with aluminium and teflon: Weinhold et al. (1980)). Recently, Hsiao and Chen (1990) were able to induce transcrystallization in various polymer/fiber pairs by simply immersing one end of the fiber in cool water. They pointed out that the ratio of thermal conductivity between carbon fiber and most polymeric matrices is about 1000. Thus, upon cooling, heat is dissipated more readily in the fiber than in the matrix and a surface gradient appears which favors transcrystallization. It is important to note that this effect will be significant only if this transient temperature gradient is comparable in time to the induction period for massive nucleation to occur. Therefore at high crystallization temperature where the induction time is large, one should not expect such a short lived gradient to have any effect. The importance of this induction time is discussed in more details in Sec. 8.6. A special case of transcrystalline morphology was recently reported by Ishida and Bussi (1990a) who reported a banded transcrystalline zone for high cooling rate in ultra high modulus polyethylene fiber reinforced polyethylene composites (Fig. 8.6). This morphology was detected through the presence of extinction lines in the transcrystalline zone parallel to the fiber direction. Banded structure results from cooperative twists of the lamellae induced by the presence of thermal stresses (Bassett (1981)).

From the above discussion it is clear that one should distinguish the effect of a temperature gradient induced during severe quenching - which favors transcrystallinity - from the effect of the high cooling rate itself which tends to decrease surface nucleation. The effect of cooling rate is better understood through a study of isothermal crystallization which can be found in the work of Chatterjee and Price (1975a). They reported temperature windows for which

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they observed transcrystallization in 43 polymer/substrate pairs. They found that the propensity to transcrystallize decreases with increasing crystallization temperature; at 130°C, isotactic polypropylene in contact with isotactic polystyrene exhibited transcrystallinity whereas the morphology was spherulitic at 135°C. This effect was attributed to the reduced nucleation rate at smaller supercooling, as predicted by Eq. (8.9). A similar observation was made by López and Wilkes (1989) who observed transcrystals at 200°C but not at 240°C in carbon fiber reinforced poly(p-phenylenesulfide) composites. This was however attributed to a steeper thermal gradient across the fiber/matrix interface as the supercooling increases. In contrast, Fitchmun and Newman (1970) observed the opposite effect for polypropylene in contact with aluminum: at 125°C the morphology was spherulitic whereas at 130°C a transcrystalline layer was observed.

However, these two very different observations are not contradictory. Looking back at Eq. (8.9), one can see that the surface nucleation rate can be expressed as a function of $\Delta\sigma$ and ΔT:

$$I_s = K \cdot \exp\left(-\frac{a\,\Delta\sigma}{T\Delta T^2}\right)$$

(8.11)

where a and K are two positive constants. Similarly, for bulk heterogeneous nucleation:

$$I_b = K' \cdot \exp\left(-\frac{a\,\Delta\sigma'}{T\Delta T^2}\right)$$

(8.12)

where K' is a positive constant. Thus:

$$\frac{I_s}{I_b} = K'' \cdot \exp\left[\frac{a\,(\Delta\sigma' - \Delta\sigma)}{T\Delta T^2}\right]$$

(8.13)

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where K" is a positive constant. It has been shown previously (see Tab. 8.1) that when surface heterogeneous nucleation is favored, $\Delta\sigma$ is smaller than $\Delta\sigma'$. Therefore one can rewrite Eq. (8.13) as:

$$\frac{I_s}{I_b} = K'' . \exp\left[\frac{b}{T\Delta T^2}\right]$$

(8.14)

where b is a positive constant. Since $1/T(\Delta T)^2$ increases with decreasing ΔT, it can be seen that I_s/I_b increases with increasing crystallization temperature, i.e surface nucleation becomes more favorable at smaller supercooling. Therefore, even though both rates decrease with increasing temperature, their relative magnitude is such that transcrystallization is favored and will be observed provided that the absolute value of the surface nucleation rate is still high enough. One can postulate that in the study of Chatterjee and Price (1975a), I_s was too small at higher temperature whereas in the study of Fitchmun and Newman (1970) I_s was large enough even at higher temperatures so that the system could fully take advantage of a lower $\Delta\sigma$.

The influence of temperature during pre-melting has also been mentioned as affecting subsequent crystallization. Numerous studies have shown that incomplete melting of polymers leaves crystalline embryos that can later serve as growth centers. A higher pre-melting temperature for a longer time will destroy many of these heterogeneous embryos thus reducing heterogeneous nucleation in the bulk matrix. In this way, transcrystallization is favored because there is less competition from the matrix. Experimentally this was observed by both Fitchmun and Newman (1970) and Weinhold et al. (1980). It might be argued that any pre-melting treatment should equally destroy the surviving nuclei at the substrate surface. However, these nuclei are more stable

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due to the presence of the surface. Some chains may also be trapped in microcracks at the surface and thus conserve some kind of order throughout the melting step. Lastly, the inherent nucleating ability of the substrate should not be affected by premelting.

8.3.2 Physicochemical Parameters

It has been shown previously that surface induced nucleation is favored when the free energy difference function $\Delta\sigma$ is minimum. From Eq. (8.2) and Eq. (8.3), for a system where dispersion forces are predominant:

$$\Delta\sigma = (\gamma_c^{1/2} - \gamma_s^{1/2})^2 + (\gamma_c^{1/2} - \gamma_m^{1/2})^2 - (\gamma_m^{1/2} - \gamma_s^{1/2})^2 \tag{8.15}$$

which can be rewritten as:

$$\Delta\sigma = 2 \cdot (\gamma_c^{1/2} - \gamma_s^{1/2}) \cdot (\gamma_c^{1/2} - \gamma_m^{1/2}) \tag{8.16}$$

For a given polymer, i.e where γ_c (crystal) and γ_m (melt) are known, Eq. (8.16) predicts that $\Delta\sigma$ approaches zero for a substrate which satisfies $\gamma_s = \gamma_c$. A trivial case is that of secondary nucleation, that is crystal growth on its own nuclei. Nonetheless it is possible, at least in principle, to predict qualitatively whether or not heterogeneous nucleation is favored once all surface tensions are known. Alternatively Eq. (8.16) should be helpful in selecting a proper substrate. The expression given for $\Delta\sigma$ can be further modified to include a polar component to the surface tension if necessary. This polar component can be related more specifically to the presence of particular groups at the surface (surface chemistry). López and Wilkes (1989) found an inverse relationship between the nucleating efficiency of various types of carbon fiber toward poly(p-

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phenylenesulfide) and the value of the polar component of the surface energy. The same effect was observed when, for a given fiber, this value was modified through anodization. They proposed that interaction between the low polarity poly(p-phenylenesulfide) and carbon fiber are enhanced when the value of the fiber polar component is decreased.

A chief objection to the surface energy approach, however, is that it is cast in terms of parameters which are not always easily accessible. In order to be useful Eq. (8.16) requires precise values of the surface tensions because it tends to diverge mathematically. Moreover, when surface energy data are given in experimental studies, there is often no mention of any differences between the melt state and the crystalline state and a commonly accepted value from the literature is often applied. Such a simplification can lead to error in the interpretation when comparing this value to that of the substrate. In particular it has been shown by Schonhorn and Ryan (1966) that there is a considerable difference between the surface tension of polyethylene single crystals ($\gamma_c = 66$ dynes/cm) and that of a completely amorphous surface layer ($\gamma_m = 36$ dynes/cm). This difference also indicates that the substrate should be equally well characterized if comparison of nucleating ability are to be based on surface energy considerations. In particular it is clear from the work of Schonhorn and Ryan (1966) that the degree of crystallinity of the substrate should be determined. It would also appear, due to the high value generally obtained for single crystals that a high surface energy substrate is desirable. Indeed it has been claimed in early investigation of transcrystallization that a high energy substrate is a necessary condition. Schonhorn (1966) noted that low energy surfaces such as polytetrafluoroethylene seem to be ineffective nucleating agents. However transcrystallization has been observed by other workers for

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polymers in contact with low energy surfaces (Chatterjee and Price (1975a);
Fitchmun and Newman (1970)).

Schonhorn (1966) also studied the connection between wettability and
surface morphology and pointed out that in order for high energy surfaces to be
fully effective, sufficient time must be allowed to achieve intimate contact with
the surface. The importance of the true surface of contact leads to another
characteristic of the substrate whose influence has been generally ignored; its
roughness. On one hand, a rough surface might be more difficult to wet at the
microscopic level but on the other hand, it also provides such high energy
features as dislocations which favors heterogeneous nucleation. López and
Wilkes (1989) found a correlation between the roughness of their carbon fibers
(as determined by scanning electron microscopy) and their nucleating ability
toward poly(p-phenylenesulfide). Thus determination of the substrate specific
area by gas adsorption technique seems advisable.

Another problem with Eq. (8.16) is that it does not recognize the
influence of lattice matching. The importance of lattice matching has been
stressed very early by Turnbull and Vonnegut (1952) who predicted, based on
theoretical considerations, that the nucleating efficiency should be inversely
proportional to the degree of disregistry, δ, between the substrate and polymer
unit cell. They further related the free energy of phase transition to a function of
δ. Binsbergen (1973) modified Eq. (8.16) to account for lattice matching and
contributions other than those arising from dispersion or polars forces:

$$\Delta\sigma = 2 . (\gamma_c^{1/2} - \gamma_s^{1/2}) . (\gamma_c^{1/2} - \gamma_m^{1/2}) + (1 - \xi) . \varepsilon_\gamma \qquad (8.17)$$

where ξ is defined as an accommodation coefficient of value $0 < \xi < 1$ and ε_γ
refers to other contributions. For perfect lattice matching, $\xi = 1$. Eq. (8.17)

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indicates that in order to promote the transcrystallization of a given polymer one can manipulate two variables: the surface energy of the substrate and the degree of lattice matching.

In a study of carbon fiber reinforced polypropylene, Hobbs (1971) observed a drastically different nucleating ability between fibers with large graphite planes that are highly oriented along the fiber axis (type I fiber) and fibers with small and disoriented graphite planes (type II fiber) (Fig. 8.7). Whereas type II fibers show general absence of nucleation under the microscope, extensive transcrystalline growth was observed under the same thermodynamic conditions for type I fiber. Using a molecular model, Hobbs (1971) showed that the hydrogen atom of the helical polypropylene chain can be placed in contact with the low energy sites (C-C bonds) of the substrate. Such a process requires long range regularity of the adsorption plane which is found only in type I fiber. Hartness (1984) arrived to a similar conclusion in a study of carbon fiber reinforced poly(ether-ether-ketone) composites. Theoretical calculations by Baukema and Hopfinger (1982) showed that the parallel orientation of polyethylene on the basal plane of graphite single crystals was energetically favored. In a study of adsorption of n-alkanes onto graphitized carbon black and various ground graphites, Groszek (1970) found that the adsorption was confined entirely to the basal planes of graphite crystals.

Lattice matching seems to be a predominant parameter as indicated by the recent work of Hsiao and Chen (1990). They first observed that poly(p-phenyleneterephtalamide) (PPDT) fibers could induce transcrystallization of poly(ether-ether-ketone), poly(phenylenesulfide) and poly(phenyleneoxide) which was explained by the fact that these polymers and the fiber have very similar a and c unit cell dimensions. More importantly, they were able to induce transcrystallization of these polymers by coating previously inactive glass and

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polyacrylonitrile-based carbon fibers with PPDT. In Sec. 8.5, it is shown, based on mechanical properties considerations, that it might be desirable to induce transcrystallization. Coating of the reinforcement with a substance which accommodates the lattice of the crystallizing polymer might therefore be of great practical importance.

Other researchers have suggested that transcrystallinity is affected by the substrate surface chemistry and namely by chemical similarity between the substrate and the crystallizing polymer (Fitchmun and Newman (1970); Gray (1974a)). The influence of particular chemical groups can be studied in two methods. First, one can relate the nucleating ability to a measure of the surface tension and look for a correlation between the value of the polar component of the surface tension, the presence of certain chemical groups and the propensity to induce surface nucleation. Another approach is to study the effect of well characterized heterogeneities on the degree of supercooling necessary to observe massive nucleation. Extensive data have been compiled for seeded polypropylene melt by Beck (1967) for more than 150 nucleating agents. The chemical structure of the seeds was found to indeed strongly affects the crystallization temperature. The characteristic crystallization temperature, T_p, for sodium benzoate seeded polypropylene melt was 131°C whereas that for pure polypropylene was 106°C. Beck (1967) proposed that a good nucleating agent for polypropylene should consist of two parts: an organic part which helps to solubilize the heterogeneity in the melt by reducing the interfacial surface free energy and a polar group which ensures that the heterogeneity is still solid in the melt at all temperatures. Even though Beck (1967) could discern some trends (influence of tert-butyl groups, of aromatic organic groups, of carboxylic acids salts,etc.) it is still very difficult to tell exactly what makes a particular nucleating agent so effective based on its chemical structure alone.

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8.3.3 Presence of Stresses at the Substrate/Melt Interface

The relationship between stress and crystallization has been long recognized through the investigation of various phenomena: row nucleation in injection molded thermoplastics and shear induced nucleation in dilute polymer solution or stress induced crystallization in elastomers. Stresses present at the fiber/matrix interface can be mechanically or thermally induced, but they result in the same effect; the orientation of the polymer molecules near the fiber surface. The entropy of the oriented melt is reduced, and there will be an additional decrease in the free energy. Thus the melting temperature and the degree of supercooling are enhanced. Gray (1974b) studied the effect of mechanical stresses on glass fibers reinforced polypropylene melt. When one of the two mutually perpendicular glass fibers was gently pulled, a transcrystalline region was observed under the microscope immediately along its length, whereas nucleation did not occur on the undisturbed fiber. The appearance of this transcrystalline zone was similar to that observed in a polymer/substrate pair where transcrystallization occurs without shear. Gray (1974b) also showed that the stress does not need to be external and can be self-generated. For example, thermal contraction of air bubbles upon cooling of the melt produces stresses at the air/polymer interface and results in crystallization. In technological processing of fiber reinforced thermoplastics, stress induced transcrystallization must be considered because flow will occur in the matrix prior to crystallization. Misra et al. (1983) found that the appearance of transcrystallization in injection molded glass fiber reinforced polypropylene depends on a minimum fiber weight fraction (i.e the availability of internal stresses) on the order of 35%. They also noted that the extent of the

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transcrystalline zone was greater in the case of samples molded at lowest pressure, as low injection pressure leads to high internal stress. Kubat and Rigdahl (1975) have shown that internal stresses develop in the sample during injection molding. Addition of fibers will cause localized perturbations in the flow field. Mackley (1975) analyzed the flow past a fiber and showed that along the symmetry axis of the fiber an extensional flow field can be generated with very high extension rate near the tip. Shearing flow also exists over the side surface of the fiber. This flow pattern suggests that transcrystallization should be seen not only at the fiber/matrix interface but also as a "tail" in the region where the fiber was pulled out of (Fig. 8.8). This phenomenon was observed experimentally by Burton et al. (1984) in injection molded bars of carbon fiber reinforced polypropylene and recently by Thomason and Van Rooyen (1990) in aramid fiber reinforced polypropylene. In this latter work, the aramid fiber was pulled at various speeds (5-5000 μm/min) through the melt. Transcrystallization was observed even at the lowest speed, and no lower boundary in pulling speed could be determined. However, they pointed out that stresses could have been built up during the cooling phase due to a mismatch in the thermal expansion coefficient of the fiber and the melt. This large difference will tend to deform and align the polymer melt molecules near the fiber interface. They noted a correlation between the axial thermal expansion coefficient of a given fiber and its ability to induce transcrystallization. They also offered an alternative explanation to that given in Sec. 8.3.1 for the observed temperature dependency of the transcrystalline morphology; at higher crystallization temperatures, these thermally induced stresses have sufficient time to relax so that transcrystallinity is not observed whereas at lower temperatures, the molecules are caught up by crystallization while still in an oriented state.

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8.3.4 Molecular Weight

Although molecular weight is a very important parameter in polymer crystallization, little has been done to investigate its effect on transcrystallization. Moreover, there appears to be some controversy on its effect in the literature. Molecular weight is of particular interest because it influences the crystallization temperature (i.e the nucleation rate) as well as other properties including wetting and viscosity. The wetting behavior influences the energetics at the interface whereas the viscosity influences the processing conditions. Additionally the polydispersity of the sample is also a factor because it leads to a distribution of crystallization temperatures. In this case, the higher molecular weight fraction may serve as a nucleating agent for the lower molecular weight material. Lastly, molecular weight also influences the final morphology of the sample, because it controls in part the size of the spherulites. Recently Ishida and Bussi (1990a) studied the transcrystallization of a polyethylene fiber reinforced linear high density polyethylene and recorded the transcrystallization temperature for several molecular weight fractions and under various cooling rates. As expected, the transcrystallization temperature decreases with molecular weight (5°C decrease from 31,300 to 3,300 in molecular weight). For the larger chains, less configurational entropy is lost during the phase transition. This smaller loss corresponds to a lower value of the free energy for a critical nucleus (or to a smaller volume) and therefore to a higher crystallization temperature. For the lowest molecular weight fraction, the morphology in the matrix changes from mature spherulites to immature spherulites (sheaf-like spherulites). Namely, growth occurs along diverging radial fibrils before filling the space uniformly. In this case, the transcrystalline zone is expected to show a lesser degree of order and to contain more defects.

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In particular, the transcrystalline growth front appears to be less regular in this case than for the unfractionated polymer. Similarly, Thomason and Van Rooyen (1990) studied the transcrystallization of two polypropylene samples with different melt indices, i.e different molecular weight. Although both samples exhibited the same temperature dependency for the transcrystalline growth rate, the maximum temperature at which transcrystallization was observed changed from 138°C for the low molecular weight fraction to 146°C for the high molecular weight fraction. They postulated that the relaxation time for the thermally induced stresses was larger in the case of the higher molecular weight material. Therefore stress induced orientation of the polymer chains near the fiber surface can exist at higher temperature and give rise to transcrystallization. Thus it appears that at a given crystallization temperature there is a minimum molecular weight below which transcrystallization will not be observed.

However this view is in apparent contradiction with the results reported by López and Wilkes (1989) who studied carbon fiber reinforced poly(p-phenylenesulfide) composites. They found that, under the same thermodynamic conditions, transcrystallization occurs in the lower molecular weight poly(p-phenylenesulfide) (Mw = 32,000) whereas no surface nucleation is observed for a higher molecular weight material (Mw = 63,000). Because an earlier study showed that the bulk nucleation density is greater for the higher molecular weight polymer, they speculated that the absence of transcrystallinity in their higher molecular weight sample is due to the increased competition from the matrix. This view is supported by the work of Folkes and Hardwick (1984) who also found an upper limit in molecular weight above which transcrystallization disappears in polyester fiber (Terylene) reinforced polypropylene composites. Assuming that nucleation is initiated at the attachment point of the polypropylene chain-ends to the fiber, they postulated

that the observed effect is related to the decrease in chain-ends concentration as molecular weight increases. Moreover, as higher molecular weight chains have a restricted mobility due to entanglements, they are also less available for rapid crystallization at the fiber surface.

An interesting possibility was mentioned by Lovering (1970) who observed the transcrystallization of a *trans*-1,4-polyisoprene in contact with a piece of teflon or aluminum foil. He tentatively assigned the presence of a transcrystalline zone to segregated low molecular weight material. He also noted that fractions with molecular weight in the 50,000 - 70,000 region showed the greatest propensity to transcrystallize. This concept of a region would reconciliate the partisans of an upper or lower limit. The idea of molecular weight segregation merits some more consideration and experimental work in light of the molecular weight dependency of the surface tension (Legrand and Gaines (1969)):

$$\gamma = \gamma_\infty - \frac{k}{M_n^{2/3}}$$

(8.18)

where γ_∞ is the extrapolated infinite molecular weight surface tension, k is a positive constant and M_n is the number-average molecular weight. As mentioned earlier, the surface free energy of the substrate has been considered as an important parameter influencing the appearance of transcrystallinity. It was shown earlier that heterogeneous nucleation is favored when the free energy difference function is minimized. This free energy difference function depends on the surface free energy of the different components in the system (substrate, melt and polymer crystal). Therefore, there might be a range of molecular weights which minimize the value of this function and leads to selective adsorption of a particular fraction onto the substrate.

8.4 Experimental Techniques for Studying Transcrystallization

8.4.1 Optical Microscopy and Scanning Electron Microscopy

Optical Microscopy (OM) has been by far the most widely used experimental technique because transcrystallization is easily discernible. The scale of observation is usually sufficient to study a typical transcrystalline zone whose thickness is on the order of a few tens of micrometers. The requirements are quite simple; an optical microscope equipped with cross polarizers, since the transcrystalline zone is birefringent, and a good quality objective lens. Since growth and nucleation are highly temperature dependent, a hot-stage with good temperature control is also desirable. Composite films are usually prepared in the following way; the polymer matrix is first cast from solvent to produce a thin film with uniform thickness; the solvent is then evaporated and the fiber is deposited onto the molten film. Care must be taken to avoid orientation effect and stresses during the casting process since it can affect crystallization. Similarly one should ensure thermal equilibrium and avoid the presence of thermal gradients at the film surface.

Barriault and Gronholtz (1955) used polarized light microscopy to study the birefringence of crystalline and transcrystalline regions. Within experimental error they found a common value, of the order of 0.01. By comparing this value to the theoretical spherulite radial birefringence, they concluded that it was not likely that the polymer chains were oriented radially in the transcrystalline zone. On a more quantitative level, the transcrystalline growth rate has been

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monitored by OM to yield some of the interfacial energy parameters introduced in Sec. 8.2.2. However the magnification and the resolution of a typical optical microscope are not high enough so that the individual nucleation sites at the fiber surface can be recognized. In fact in OM, one draws conclusions on the nucleation density and on the possible nature of the nuclei from the macroscopic effect that these microscopic nuclei have on the texture. Thus, recently several studies have used scanning electron microscopy (SEM) as a characterization tool to gain further insight into the nucleation sites. Besides enhanced resolution, SEM also enables observation of fracture surfaces following mechanical testing in order to asses the quality of the adhesion at the fiber/matrix interface. Peacok et al. (1986) studied the etched cross section of carbon fiber reinforced poly(ether-ether-ketone) composites by SEM. Because there is preferential etching of the amorphous region, crystalline features are highlighted. They found that nucleation predominantly occurs at the fiber surface, producing full fan-like half spherulites. Two types of nucleation sites were recognized; nucleation from discrete, well separated points on the fiber surface and nucleation between very close fibers (i.e where a thin polymer layer is sandwiched between two nearly touching fibers). It was postulated that nucleation is favored in these regions because thermally induced stresses are larger there. It can also be seen in Fig. 8.9 that, although fiber induced nucleation dominates the morphology, the nucleation density is not high enough such that transcrystallinity is observed. Recently, Guigon et al. (1989) studied the heterogeneous crystallization of pultruded glass fiber reinforced polyamide rods, both parallel and perpendicular to the fiber direction. They found marked differences in morphology as a function of the observation distance to the center of the rod. Near the axis of the rod, spherulitic growth was observed initiating from glass fibers. The surface nucleating density in this region was estimated to

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be in the range 0.05-0.20 nuclei/μm^2. Near the surface of the rods where the stress level, the flow induced orientation, and the temperature gradient are expected to differ, a transcrystalline morphology was observed. After a flexural test, separation between the bulk matrix and the transcrystalline zone was observed whereas adhesion was maintained at the fiber/transcrystalline zone interface. This test suggests an improvement in adhesion due to transcrystallinity.

8.4.2 X-ray Techniques

X-ray diffraction patterns provided, in a very early period of transcrystallization research, the first indications that the transcrystalline layer was oriented. An isotropic polymer sample will scatter X-rays to give diffraction rings, whereas an oriented sample will give rise to arcs. Using X-ray microbeam analysis of cross sections of polyamide 66 transcrystalline films with the sample surface oriented parallel to the equator, Barriault and Gronholtz (1955) found that the patterns were always oriented with the reflection from the H-bond sheet on the equator. They concluded that on the average the polymer chains were parallel to the surface and that the H-bonds were parallel to the normal surface. Eby (1964) also confirmed that the b-axis of the chains was mainly normal to the surface in transcrystalline polyethylene films.

One of the advantages of the X-ray technique is its unique ability to distinguish simple transcrystallization from melt epitaxy. Indeed in the interpretation of mechanical testing data, it is important to know whether the a and c axis are isotropically distributed at the substrate surface plane or have a preferred orientation. Moreover it is also possible to evaluate the degree of crystallinity as well as the average crystallite size from an X-ray diffractogram.

It is therefore possible, in principle, to estimate the thickness of the transcrystalline lamellae as a function of the crystallization conditions and to see if there is any difference with the lamellae thickness in the bulk matrix. The degree of crystallinity of the ordered transcrystalline structure could also be compared to that of the bulk matrix. Unfortunately, such a study has not been undertaken to the authors' knowledge. The X-ray diffractogram is also very sensitive to the presence of an oriented surface layer. Lovering (1970) showed that reflected X-rays are a convenient and rapid way to detect transcrystallinity. In the case of transmission, the transcrystalline layer has little or no effect because the information is blurred by the unoriented material. Transcrystallinity strongly affects the relative intensity of the diffraction peaks (Fig. 8.10) and Lovering (1970) suggested that it might be possible to estimate the amount of transcrystallinity by taking ratios from selected peaks. Using reflection X-ray, Clark and Starkweather (1962) were able to assign specific reflections to the oriented transcrystalline layer in a polytetrafluorethylene film by comparing the diffractogram of the initial film with that of a film where the surface layer had been removed.

8.4.3 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a useful tool because it enables isothermal crystallization study as well as kinetic study. The extent of crystallization as a function of time can be recorded and using the Avrami analysis (reviewed in Schultz (1974))) information on the nucleation process can be obtained. It enables one to estimate the degree of crystallinity of the polymer sample, which can then be compared to the value obtained by X-ray. The DSC thermogram is also very sensitive to the presence of heterogeneous

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nucleating agents. Kantz and Corneliussen (1973) found that in glass fiber reinforced polypropylene, the crystallization exotherm is bimodal, thus indicating the occurrence of two types of nucleation events. The upper crystallization temperature (124°C) was assigned to fiber induced crystallization whereas the lower temperature exotherm (117°C) corresponds to the bulk matrix. It was also shown by Camaro et al. (1988) and by Lee and Porter (1986) that surface induced crystallization is substantially enhanced when embryos in the bulk matrix have been eliminated by premelting at high temperature prior to crystallization. This observation is consistent with the OM observations of Fitchmun and Newman (1970).

DSC thermograms of composites films exhibiting transcrystallization have been studied but the results are sometimes conflicting. Recently, He and Porter (1988) have used DSC to study transcrystallization in ultra-high modulus polyethylene fiber reinforced polyethylene composites. They observed a shoulder at 130°C in the main melting endotherm of the polyethylene matrix (132°C). This shoulder was attributed to the melting of the transcrystalline zone. A similar effect was reported by Matsuoka et al. (1968) for transcrystalline polyethylene films obtained by compression molding between copper sheets. They observed an even greater difference in melting point, on the order of 5°C and found that the heat of fusion for the transcrystalline zone was about 20 % lower than that for a regular spherulitic film. The lower heat of fusion suggests that the degree of order in the transcrystalline zone, or the degree of crystallinity, is lower than that of the more common bulk morphology. The lower melting point suggests that the crystallites are thinner in the transcrystalline zone. The melting point of a lamellae of unit thickness, l, depends on the fold surface free energy, the heat of fusion and the equilibrium melting temperature in the following way:

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$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta h_f \, l} \right)$$

$$(8.19)$$

One can also show that the initial lamellae thickness depends on the degree of supercooling, ΔT (Hoffman et al. (1976)):

$$l = \frac{c_1}{\Delta T} + c_2$$

$$(8.20)$$

where c_1 and c_2 are approximately constant. He and Porter (1988) also showed that, in a constant cooling rate experiment, transcrystallization produced a shoulder at 124°C, about 2°C higher than the temperature at which the bulk matrix crystallizes. An isothermal crystallization experiment further confirmed that transcrystallization occurs prior to bulk crystallization (Fig. 8.11).

Since transcrystals are nucleated prior to bulk spherulites, i.e at lower supercooling ΔT, Eq. (8.20) suggests that the transcrystalline lamellae thickness should be greater than that of a bulk spherulite. Therefore the transcrystalline zone should melt after the bulk matrix.(see Eq. (8.19)) and not before as it has been observed. Three explanations can be offered for this apparent discrepancy. First the possibility that the true temperature at the fiber surface is lower than that in the bulk matrix must be considered because the heat is better dissipated by the fiber than by the matrix. Consequently, the true supercooling at the fiber surface is greater than that recorded and l is in fact lower than predicted. Thus upon melting, the transcrystals will disappear before the bulk spherulites. The second possibility is to assume that the supercooling is uniform throughout the sample but that the lower lamellae thickness arises from crowding of the nuclei at the fiber surface. It is indeed possible that, because of the high nucleation density at the fiber surface, the nuclei quickly impinge on

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each other and therefore cannot achieved their equilibrium dimensions as predicted by the theory. In the case of polyethylene/polyethylene composites melt epitaxy is a distinct possibility. It would thus be relatively easy to nucleate at the fiber surface and the transcrystal thickness could be lower than expected due to a crowding effect. Last the lower melting point could be due to low molecular weight material which has been selectively adsorbed for interfacial free energy reasons.

The degree of crystallinity of the transcrystalline zone is another point of interest. Indeed it has been observed by He and Porter (1988) that the overall degree of crystallinity increases as the fiber fraction increases, i.e as the amount of transcrystals increases. This result suggests that either the presence of fiber allows more material to crystallize or that the degree of crystallinity in the transcrystalline zone itself is higher. This latter possibility is in accordance with the simple idea that this zone possesses, *a priori*, a higher degree of orientation due to a likely epitaxial effect. However this contradicts the earlier findings on the heat of fusion of Matsuoka et al. (1968). A possible explanation is that, upon nucleation and growth of the transcrystals, considerable uncrystallized material is trapped between transcrystals. Thus the overall degree of crystallinity is lowered. The lower heat of fusion could also be due to the presence of low molecular weight at the interface. The concentration of chain ends, which can be viewed as defects, is higher for low molecular weight, and therefore the heat of fusion is lowered. In any case it remains that more experimental data are needed until one can provide an unambiguous answer to these two challenging questions.

So far, DSC experiments have been analyzed in terms of lamellae thickness and heat of fusion. However DSC has also been used to study the

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development of crystallinity with time. This type of study is based on the Avrami equation:

$$1 - \chi(t) = \exp(-k\, t^n)$$

(8.21)

where $\chi(t)$ is the fraction of crystallized material at time t and k is a constant at a given temperature. The Avrami exponent n can take values ranging from 0.5 to 4 depending on the growth geometry (rod, disk or sphere), the nucleation mode (simultaneous or sporadic), and the rate-controlling process (interface or diffusion control). This is an attractive approach in order to evaluate the effect of the introduction of fibers on the overall crystallization kinetic. The value of n for a composite sample is expected to differ from that for the pure matrix because of surface induced nucleation and restricted growth due to the presence of fibers. The Avrami equation is used for data acquired in isothermal experiments but it has been adapted by Ozawa (1971) to the case of non-isothermal study (at constant cooling rate). Recently, Echalier and Davis (1989) have studied glass fiber reinforced polypropylene composites exhibiting transcrystallization at various cooling rates (from 5°C/min to 40°C/min). They found a value of $n=2$ compared to $n=3$ for pure polypropylene. However they could not attribute this decrease solely to the change in growth geometry (from spherulite to disk). It should be noted that they did not mention the ratio of transcrystalline material to bulk spherulitic material. Changes due to growth geometry should be more noticeable for samples with very large transcrystals. Interpretation of the results must be very careful as deviations from the theory are observed when Ozawa's approach is applied to composites: slowing down of the crystallization kinetic at high degree of conversion and continuous increase of n with temperature. As a consequence, the experimental data often

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tend to depart from the theoretical equation at high fractions of crystallized material. These problems arise because the Avrami equation was not developed for composites. Therefore, it does not take into account the geometrical constraints of such systems.

An interesting alternative approach has recently been taken by Billon et al. (1989) who used numerical simulation to study the effect of restricted space on the value of the Avrami coefficient. Crystallization was simulated in a two dimensional film with and without surface nucleation. It was shown that the crystallization kinetic is slowed down when the available space decreases and that crystallization is substantially enhanced by surface nucleation. Both these phenomena contributed to changing the value of the Avrami exponent.

8.4.4 Dynamic Mechanical Spectroscopy

Dynamic mechanical spectroscopy (DMS) is a very powerful and versatile tool because it allows not only a study of bulk properties such as the elastic or the loss modulus but also observation of phenomena occurring at the molecular level including molecular transitions and relaxations or chemical degradation. Commercial apparatus now enable one to investigate a wide range of frequencies, temperatures, and sample geometry and offer multiple tests procedures (dynamic or steady state tests, relaxation and creep measurements) for materials as different as polymer melts, rigid solids, composites systems, low viscosity liquids or reactive systems.

Matsuoka et al. (1968) studied the molecular relaxations of transcrystalline polyethylene films. They found that, at all temperatures, the transcrystalline material exhibits a higher loss factor, tan δ. Since the elastic part of the modulus also increases, this increase is mostly due to the much higher

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value of the loss modulus. They postulated that this change in tan δ is either due to a greater amount of non-crystalline regions within the transcrystalline structure or to peculiar but unresolved interactions between the transcrystalline lamellae. The transcrystalline material also exhibited a supplemental transition, α', found above 80°C, which was absent in the spherulitic sample. They also noted marked differences in the low temperature region (-80°C to -160°C). A γ transition is observed at -140°C for the transcrystalline material whereas a broader dispersion is seen at -125°C for the bulk sample (Fig. 8.12). The interpretation of the data is complicated in this case by the fact that there is still controversy on the nature and the mechanisms associated with polyethylene transitions found in this region (Boyer (1977)). They concluded that the -140°C peak is associated with defects confined within the crystals while the -110°C peak is a secondary transition of the amorphous glassy region. However, DMS results cannot be interpreted solely in terms of orientation. Indeed, the study of single crystal mats has revealed that the crystal thickness strongly affects the magnitude of relaxation peaks. This particular study is beyond the scope of this chapter; however, an excellent review is available on the subject (Ferry (1980)).

Finally, it should be emphasized that the DMS data available on transcrystallinity were obtained only for films. In the case of fiber reinforced thermoplastic composites, one might expect additional effects on the dynamic mechanical spectrum due to restricted motion of the adsorbed chains at the interface. A priori, one would therefore expect the glass transition temperature to be shifted to higher temperature and the activation energy for this process to increase. However, until experimental data are available for composites, this must be just considered as a possibility. This lack of experimental data is not an accident and is rather revealing on the nature of the difficulties encountered in the characterization of transcrystallinity by DMS. Indeed, for DMS results to be

meaningful, the behavior of a transcrystalline system must be compared to that of a system where there is no or little transcrystallinity. This assumes that the extent of the transcrystalline zone can be controlled in a systematic way. Studies by other techniques such as DSC would also be made easier if almost entirely transcrystalline composite samples could be produced without having to use a high fiber content. These kind of experimental necessities is the reason for more quantitative studies aimed at controlling the morphology.

8.4.5 Infrared Spectroscopy

Infrared Spectroscopy (IR) has long been recognized as a valuable analytical tool in the study of polymeric materials because of the wealth of informations provided on the conformation, orientation, hydrogen bonding, molecular symmetry, and crystal forms in the sample. With the advent of Fourier Transform Infrared Spectroscopy (FTIR), a considerable gain in sensitivity over regular dispersive spectroscopy has been achieved. This enhanced sensitivity enables one to detect surface regions with low signal intensity or even very thin layer of adsorbed material. FTIR is particularly useful for the study of surface layers as specific techniques can probe a predetermined thickness in the surface region or obtain information on the specific orientation of adsorbed species on a substrate. Moreover, these techniques are amenable to quantitative analysis.

Luongo and Schonhorn (1968) have used Attenuated Total Reflection (ATR) spectroscopy to characterize the surface region of polyethylene films nucleated on various substrates. By using ATR they were able to selectively probe the surface region ($\approx 2\mu m$). From the ratio, $R_{720/730}$, of the intensity of the crystalline bands at 720 cm^{-1} and 730 cm^{-1}, the degree of crystallinity in the

surface region was measured. They found that the surface region of a polyethylene film nucleated on a high surface energy substrate (gold) was more crystalline that that of a film nucleated on a low surface energy substrate (polytetrafluoroethylene). By studying the dependency of $R_{720/730}$ on the angle of incidence of the IR beam with the surface, they were also able to show that the polyethylene film nucleated against polytetrafluoroethylene has a higher degree of orientation (Fig. 8.13). Another technique, Reflection absorption spectroscopy (RAS), has been used by Nguyen and Ishida (1986) to study the degree of orientation at the interface of annealed poly(ether-ether-ketone) films and graphitic substrates. For randomly oriented films (quenched), no particular orientation was observed. However it was shown, using parallel polarized light, that the carbonyl stretching frequency and the aromatic C-H out-of-plane vibrations progressively disappears as surface orientation develops upon annealing. In this particular case, the crystalline polymer chains were found to to be normally oriented to the substrate, which is rarely observed in surface induced crystallization. It was postulated that the intermolecular interactions are stronger than the interactions between the chains and the substrate. IR has also been used to characterize the changes in orientation for transcrystalline poly(vinylidene fluoride) films as well as uniaxially oriented and biaxially oriented films (Weinhold et al. (1984)).

8.5 Influence of Transcrystallinity on the Mechanical Properties of Fiber Reinforced Composites

The presence of a transcrystalline zone is expected to improve both the adhesion at the fiber/matrix interface due to a higher nucleation density and the

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mechanical properties of the interphase as a result of lamellae orientation. However, very few articles have been published in the literature, which address this issue. A reason for the scarcity of reports dealing with mechanical properties has been mentioned in Sec. 8.4.4. In order to provide an unambiguous answer, a sample with spherulitic matrix morphology must be compared with the exact same sample where large transcrystals are present. In general two such samples could be produced by varying the crystallization temperature and keeping all other parameters, such as the percentage of reinforcement, constant. However, this comparison cannot be valid because, while inducing transcrystallization by changing the crystallization temperature, the average size of the spherulites in the bulk matrix and the lamellae thickness are also modified. Because these two parameters are known to influence the mechanical properties, it is impossible to attribute any enhancement in properties solely to the presence of a transcrystalline zone. If such a test is to be successful, an *entirely* transcrystalline sample must be compared to a sample exhibiting no transcrystallinity. One possibility is to bring the fibers so close to each other that only transcrystals can develop. However, a higher fiber content reduces proportionally the amount of transcrystalline material studied. The danger in this case is to test the effect of fiber volume rather than the effect of transcrystals. This discussion illustrates why morphology control is of central interest. The problem described affects more the study of the interphase than that of the interface because adhesion at the interface depends little on the extent of the transcrystalline zone.

8.5.1 Adhesion at the Polymer/Substrate Interface

Much of the early work in this field was done by Schonhorn and co-workers (1964, 1968) who studied extensively the adhesion of polyethylene to various substrates. They found that the surface layer morphology strongly influences the adhesive joint strength. In a simple peeling test of bonded polyethylene/aluminum joints (Schonhorn (1964)), a relatively thick layer of polyethylene was found to adhere at the substrate surface. Optical microscopy revealed that this layer consisted of transcrystalline material. The thickness of the transcrystalline layer increased with the bond preparation time at the selected temperature. Later, Schonhorn and Ryan (1968) studied the adhesion in epoxy adhesive-polyethylene film-epoxy adhesive pieces. It was shown that the presence of a large transcrystalline surface layer in the polyethylene film considerably enhances the adhesive joint strength. From their work, it appears that the major interest of a transcrystalline layer is that it preserves the expected properties rather than bring any enhancement in itself. Indeed when no transcrystalline zone is present, a weak boundary layer is formed which decreases considerably the expected quality of adhesion. Transcrystallinity prevents such a detrimental effect by extending the bulk properties of the matrix to the surface region. If the transcrystalline zone is damaged, this protective effect is lost. Schonhorn and Ryan (1968) found that a similar result can be achieved by crosslinking the surface layer through activated species. They used an analogy between the behavior of a transcrystalline layer and that of a crosslinked layer to explain the increased cohesive strength. Because of extensive surface nucleation, there is a strong competition between the chains at the surface. Therefore it can be speculated that considerable entanglements of the chains occurs. These entanglements are very similar in effect to crosslinks.

Other workers have indicated that transcrystallinity might contribute to enhanced adhesion. Hsiao and Chen (1990) have used a microdebonding test

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on single filaments to measure the effect of transcrystallinity on the debonding force. They prepared single carbon fiber/poly(ether-ketone-ketone) (PEKK) specimens with and without transcrystallinity. Transcrystallinity was induced by two methods: coating the fiber with a substance whose unit cell dimensions are similar to that of the PEKK matrix, and immersing the fiber end in a water bath so that a temperature gradient could develop at the fiber surface. The presence of a transcrystalline zone led to a 20% increase in debonding force in the first case and to a 30% increase in the second case. One problem with this type of test, however, is that the uncertainty of the measurements is quite high (35%). Hsiao and Chen (1990) also found that the positive effect of transcrystallinity decreases as the fiber volume increases. As the fiber volume increases, the distance between fibers decreases sharply, and the transcrystalline zone becomes thinner. Consequently there is less and less differences between a regular sample and a transcrystalline sample.

Until now the adhesion has been considered only in terms of what happens directly at the fiber surface. However, in light of some recent studies, the most important phenomenon might well occur away from the surface, at the bulk matrix/transcrystalline zone interface. Recently, Guigon et al. (1989) studied glass fibers/polyamide composites by SEM and found that failure after flexural test occurs at the bulk matrix/transcrystalline zone interface rather than at the fiber/matrix interface (Fig. 8.14). The importance of this second interface has been generally ignored. A more complete picture of a fiber reinforced composite system incorporating this interface is presented in Fig. 8.15. A similar observation was made earlier by Lee and Porter (1986) who studied the crystallization of PEEK in carbon fiber composites. They also measured the transverse tensile strength of PEEK/carbon fiber composites. Samples exhibiting high surface nucleation were found to have a much higher transverse

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tensile strength than the strength predicted by a model assuming no interfacial adhesion. The fracture toughness was also greatly increased. A very elegant explanation for these results was provided based on the theory of Keith and Padden (1963).

Keith and Padden (1963) recognized that polymer melts contains numerous defects which can acts as impurities: atactic species, branched or entangled molecules, and chain ends. They showed that during crystallization these impurities diffuse away from the crystal growth front. Eventually, the concentration of such impurities become quite high in regions where the growing spherulites impinge on each other. Consequently, some uncrystallized material remains trapped in between spherulites. This poorly crystallized zone acts as a weak point in the polymer sample. This phenomenon is of great importance in the case of fiber reinforced composites. If matrix nucleation is dominant, the uncrystallizable impurities accumulate at the fiber/matrix interface. Consequently a weak layer develops, and the adhesion is poor. However, if surface induced nucleation is favored, the transcrystalline growth front can push these impurities away from the fiber surface. At the same time, spherulitic crystallization occurs in the matrix which also tends to reject these impurities. As a result, the concentration of uncrystallizable material will be much higher at the transcrystalline zone/bulk matrix interface than in the rest of the sample, and a weak zone will develop there. Thus transcrystallinity enhances adhesion at the fiber/matrix interface by shifting the weak boundary layer toward the bulk matrix.

Krautz (1971) has shown that the improvement in properties of composites is an order of magnitude greater for semicrystalline polymer matrices than for amorphous polymer matrices. The previous discussion has shown that transcrystallization might be responsible for much of this effect.

Kardos (1973) has even proposed that preferential interfacial crystallization be preponderant in the case of difficult to crystallize engineering thermoplastics. In this later case, annealing might be of great interest to induce crystallization next to the reinforcement.

8.5.2 Mechanical Properties of Transcrystals

In polymer composites where transcrystallization takes place, the particular orientation of the lamellae is expected to influence the mechanical properties. Similarly changes in the molecular relaxations (magnitude and temperature) are expected, due to the different mobility of the chains at the polymer/substrate interface. The transcrystalline structure is highly anisotropic, which means that the mechanical properties of the transcrystals will also be anisotropic. Therefore, in comparing results obtained by various investigators, special attention should be paid to the relative orientation of the transcrystalline lamellae with respect to the direction of testing. Kwei et al. (1967) studied the influence of an oriented transcrystalline zone on the real and imaginary part of the dynamic Young's modulus, E, in polyethylene and polypropylene films. By changing the thickness of the film, they were able to vary the ratio of transcrystalline material to regular spherulitic material. Eventually, the thickness of the film was decreased to the point where the film was entirely transcrystalline. The results were interpreted using a model in which the transcrystalline zone and the bulk region produces a parallel response to the applied stress. They found that the modulus reaches an asymptotic value as the thickness is decreased which is the value of the modulus for transcrystals (Fig. 8.16). This thickness effect is not an artefact since a similar experiment for a non-crystalline epoxy system showed no change in the film properties with

decreasing thickness. A two to three fold increase in the value of the elastic and loss modulus was noted for the transcrystalline polyethylene and polypropylene films.

When the shear properties are tested, no major difference is observed between the level of the shear modulus, G, for the transcrystalline zone and that for regular spherulites (Eby and Colson (1966); Crissman and Passaglia (1966)). This observation can be rationalized as follows. What is tested in a shear experiment is the response of the weakest component, i.e the bulk matrix; the transcrystalline zone and the bulk matrix are in parallel with respect to strain. In a tensile test, the response of the strongest component is tested; the transcrystalline zone and the bulk matrix are in series with respect to strain. Moreover, even though transcrystalline lamellae are preferentially oriented perpendicular to the fiber direction, there is a randomization effect because they are also uniformly distributed around the fiber. Thus the anisotropy is reduced. In shear testing where the strain is perpendicular to the fiber direction, this effect tends to minimize the differences between an oriented and an unoriented structure.

The magnitude of the mechanical relaxation is affected by the presence of oriented material. Both Eby and Colson (1966) and Crissman and Passaglia (1966) found that, in oriented polyethylene films, the α relaxation (relaxation found above room temperature) decreases whereas the β and γ processes are essentially not affected. However it is difficult to attribute this effect solely to orientation, as the lamellae thickness of their samples was affected by the crystallization and annealing temperature chosen. As mentioned earlier (Sec. 8.4.4), lamellae thickness is known to influence the magnitude of the relaxation peak.

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Another property of transcrystals which might be of practical interest is the mode of plastic deformation. More specifically, the elongation at break for the transcrystalline zone can be expected to differ from that for the bulk spherulites when the applied strain is along the fiber direction. In particular, Campbell and Qayyum (1977) have proposed that transcrystallization leads to increased elongation at break by restraining necking of the fiber. Indeed, necking would require lateral extension of the lamellae along the a-axis, which is very unlikely. Rather, they postulated that the strain at the interface is accommodated by separation of the transcrystalline lamellae along the c-axis (which is along the fiber axis for transcrystals). This way the incidence of fracture is postponed.

8.6 The Induction Time Approach

From Sec. 8.4 on experimental techniques and Sec. 8.5 on mechanical properties, it is clear that the study of transcrystallization would be made easier and more rigorous if some method to control the extent of the transcrystalline morphology was available. To be systematic, such a method should have some theoretical basis. However, the current theory of heterogeneous nucleation has a very serious practical limitation when applied to a purely transcrystalline system; because of the large number of spherulites nucleating at the interface, the nucleation rate cannot be measured and therefore $\Delta\sigma$ cannot be obtained (Sec. 8.2.2). This difficulty explains why the characterization of the energetics of the transcrystallization process using the classical theory has been attempted in only one major study (Chatterjee and Price (1975c)). In this section, an alternative approach is presented, based on the value of the induction time.

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Because this approach might help to characterize more quantitatively the transcrystallization process, it is presented in a more detailed fashion.

8.6.1 Theoretical Basis

In Sec. 8.2.2, the temperature dependency of the rate of heterogeneous nucleation, I, has been described by Eq. (8.5). I represents a number of nuclei per unit time per unit volume. In an isothermal experiment, a constant value is predicted. Thus the number of nuclei observed under the microscope in a given volume should be linear with time and nucleation should start at $t = 0$. However this effect is not what is typically observed. Generally an 'S' shaped curve is obtained with a certain delay before the onset of massive nucleation occurs (Fig. 8.17). This delay is often called induction time, t_i, and is defined as the time intercept axis of the slope of the nucleation curve. Just as I varies with temperature so does t_i. However, these variations are of opposite direction. As the supercooling is decreased, the size of the critical nucleus becomes larger and the time required to create a stable nucleus increases. At the same time, the nucleation rate decreases. Thus, intuitively, one can assume that the induction time and the nucleation rate might be related and carry the same informations on the energetics of the system.

This relationship is of particular interest in the case of surface induced crystallization because the time at which massive nucleation occurs can still be recorded even though individual spherulites cannot be distinguished at the fiber surface. Because the absolute number of nuclei is very important the observed transition will be sharp. Thus if one can find a way to relate I and t_i, $\Delta\sigma$ could be obtained whereas I cannot be measured. Because I varies inversely with t_i,

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Ishida and Bussi (1990b) have proposed that the product of these two quantities is a constant. Mathematically:

$$I(T) \cdot t_i(T) = K = Constant \qquad (8.22)$$

This relationship holds for the boundary conditions. For infinitely long nucleation (very low supercooling), the induction time goes to infinity as the nucleation rate is almost zero, but the product of these two can still be a finite constant. Inversely, for almost immediate nucleation (very high supercooling), the nucleation rate goes to infinity as the induction time goes to zero (Fig. 8.17).

By using Eq. (8.22) and Eq. (8.9), one can see that a plot of $\ln I + \Delta\varphi/kT$ versus $1/T(\Delta Tf)^2$ or a plot of $\ln (1/t_i) + \Delta\varphi/kT$ versus $1/T(\Delta Tf)^2$ should yield a linear curve with the same slope K_i. It has been shown earlier that K_i is related to $\sigma\sigma_e\Delta\sigma$. Thus the temperature dependency of the induction time for transcrystallization to appear will yield $\Delta\sigma$. A classical nucleation rate study on the bulk matrix will yield $\Delta\sigma'$ and from this the ratio A as defined by Eq. (8.4) can be obtained. The plot of $\ln I + \Delta\varphi/kT$ versus $1/T(\Delta Tf)^2$ was first suggested by Goldfarb (1980) who however did not provide any justification for it. Ishida and Bussi (1990b) have proposed a theoretical justification for Eq. (8.22) based on the Zeldovich-Becker-Döring (ZBD) theory of nucleation (Zeldovich (1942); Becker and Döring (1935)).

Why is an induction time observed ? The nucleation rate derived earlier is a steady state nucleation rate. It is assumed that, at the crystallization temperature considered, there is an equilibrium size distribution of subcritical nuclei (embryo). Following the notations used by Frisch (1957) f(g,t) represents the distribution function of embryo of size g at time t. As suggested

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by Wunderlich (1976), this distribution can be represented by a decreasing exponential (Fig. 8.18). It is much more probable to find numerous small embryo in the melt than large embryo because the free enthalpy necessary for a large embryo to survive is greater. In an isothermal nucleation experiment the sample is generally quickly cooled down from T_i (initial melt temperature, far above the equilibrium melting point) to T_c (temperature of crystallization). The induction time $,t_i$, is the time necessary to reach the steady state distribution at T_c, $f_{s,T_c}(g)$, starting from an initial steady state distribution at T_i, $f_{s,T_i}(g,0)$. Using the ZBD theory of nucleation, Frisch (1957) showed that:

$$t_i(T) = \frac{\int_0^G [\ f_{s,T_c}(g) - f_{s,T_i}(g,0)\ ]\ dg}{I(T)} \qquad (8.23)$$

where G is the size of the embryo for which the probability of decomposition is essentially zero (G is slightly larger that g^*, the size of the critical nucleus, as defined in Sec. 8.2.2). The ZBD theory was initially derived for what is termed self-nucleation, i.e nucleation which arises in the melt from its own previously grown crystals. Partially molten, high molecular weight crystals, can serve as seeds for self-nucleation. However this theory can be applied to heterogeneous nucleation if the following remarks are made.

In the case of heterogeneous nucleation, it is assumed that the subcritical nucleus initiates at the surface of the substrate or at the heterogeneities present in the melt. This assumption is justified because it is easier for an embryo to survive on a foreign surface than in its own melt. In the case of transcrystallization, the assumption of subcritical nuclei preferentially growing at the fiber surface rather than in the melt is even more justified because of the

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particular affinity between the matrix and the fiber. Therefore, if the concentration of heterogeneities is assumed to be constant for the temperature range [T1,T2] investigated, one can write:

$$\int_0^G f_{s,T_c}(g) \cdot dg = Constant \quad , \quad T_c \in [T_1,T_2] \qquad (8.24)$$

Eq. (8.24) basically expresses that the number of particular embryo of size g can change from one temperature to the other but the total number of stable nuclei which are generated is a constant because there is only a fixed number of heterogeneities in the melt. This is equivalent to a condition of normalization for a probability. The second assumption made is that at the initial temperature T_i:

$$f_{s,T_i}(g,0) = 0 \quad , \quad g \in [0,G] \qquad (8.25)$$

When T_i is far above T_m^o and the melt is kept at this temperature for a sufficient period of time, this assumption is reasonable. This means that at temperature T_i no embryo can survive at the interface melt/heterogeneities. With these two assumptions Eq. (8.22) can be derived as follows:

$$t_i(T) = \frac{\int_0^G [f_{s,T_c}(g) - f_{s,T_i}(g,0)] \cdot dg}{I(T)} = \frac{\int_0^G f_{s,T_c}(g) \cdot dg}{I(T)} = \frac{Constant}{I(T)}$$

Hence, $$I(T) \cdot t_i(T) = K \qquad (8.26)$$

The ZBD theory has been originally applied to the study of phase transitions in gases. In a study of the condensation of droplets upon very rapid

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expansion of a gas, Kantrowitz (1951) predicted that the induction time should vary inversely as the fourth power of the degree of supersaturation which is the equivalent of the degree of supercooling in a polymer nucleation experiment. However this relationship was derived for very small induction time, on the order of 0.1 microsecond. Nonetheless, Magill (1962) used a generalized expression of the same type to study the heterogeneous crystallization of Nylon 6:

$$t_i = k \, (\Delta T)^{-n} \qquad k,n = \text{constants} \qquad (8.27)$$

He was able to fit his data with n=3 and n=7 depending on the initial melt temperature and on the final crystallization temperature. However no physical meaning was assigned to k and n, and no correlation to the surface free energy parameters was attempted.

It should be noted that there is little reference in the literature to the induction time as a way to gain information on the energetics of the nucleation process because nucleation rates can be generally measured. However another particular time, the half-time of crystallization has been used in the past to study homogeneous nucleation in the droplet experiment (Gornick et al., (1967)). It is interesting to note that in this case the equation used to correlate the nucleation rate and the half-time of crystallization is derived from the fact that there is only a fixed number of crystallizable droplets. It is an assumption similar to the one made in Eq. (8.22).

8.6.2 Application of the Theory

The goal of a theoretical approach is to obtain the value of the free energy difference function, $\Delta\sigma$, for the heterogeneous nucleation of transcrystals at the fiber surface. $\Delta\sigma$ can then be compared to $\Delta\sigma'$, the value of the free energy difference function for the bulk matrix/heterogeneities in the melt system. This way, one can judge which type of nucleation is favored, independently from the temperature. Furthermore, the nucleating ability of a given fiber toward different polymers can be quantitatively compared.

The first step in the determination of $\Delta\sigma$ involves a classical growth rate study. This step does not present any difficulties even though it is performed on the transcrystalline zone. Once nucleation at the fiber surface has occurred, growth in the matrix or in the transcrystalline zone should proceed in exactly the same way. Therefore one can apply Eq.(8.10) to the transcrystalline growth rate data and the calculated value of $\sigma\sigma_e$ should not depend on the type of crystals studied. Nonetheless it was not until recently that extensive transcrystalline growth rate data were compiled by Thomason and Van Rooyen (1990) and Ishida and Bussi (1990a,b) (Chatterjee and Price (1975b) first observed that the two growth rates were identical, but for a single temperature measurement). The thickness of the transcrystalline growth front generally increases linearly with time. Measurements on the transcrystalline zone are made more easily and more precisely since a uniform growth front is observed. This advantage is especially valuable when the growth rate is very important (high supercooling), i.e when quick focus on the growth front must be achieved.

Ishida and Bussi (1990a) selected polyethylene as a matrix because extensive data on the spherulitic growth rate were available for comparison. Moreover, polyethylene is well known for exhibiting a transition in growth regime at roughly 127 °C (Hoffman, Davis and Lauritzen (1976)) (see Sec. 8.2.2 and Fig. 8.4). Also, the ability of the transcrystalline growth rate to

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recognize this transition can be tested. For bulk spherulites the occurrence of a certain regime can be deduced from the observed morphology. At higher temperatures, axialites are observed in the polymer melt but disappear at lower temperatures. Axialites, which appear as immature spherulites with thicker and more diffuse branches, are characteristic of a regime I behavior. However this change in morphology is not seen in the transcrystalline zone. Once the transcrystalline growth rate has been recorded as a function of temperature, the analysis of the data is performed as outlined in Sec. 8.2.2. The plot of ln g versus $1/(T\Delta T)$ for polyethylene/polyethylene composites is shown in Fig. 8.19 and exhibits a regime II behavior for the first 10 temperatures. From the slope of the curve, $\sigma\sigma_e$ was calculated to be 1380 erg^2/cm^4, which is in good agreement with other independent estimates for bulk spherulites where the average value of 1310 erg^2/cm^4 has been reported (Hoffman, Davis and Lauritzen (1976)). The change in growth regime is also noticeable. The values of the growth rate at higher temperatures are believed to follow a regime I behavior where 127.3 °C would be the breaking point. Indeed the calculated slope using these points is roughly twice the value for regime II as expected from the theory. In a further study of poly(ϵ-caprolactone) /polyethylene fiber composites, Ishida and Bussi (1990b) found that the transport term becomes predominant as the crystallization temperature decreases and that the transcrystalline growth rate eventually reaches a maximum (Fig. 8.20). At higher supercooling, the melt viscosity is higher, and it becomes more difficult for the polymer chains to diffuse toward the transcrystalline growth front. Such an effect had not been revealed by a regular growth rate study on bulk spherulites (Phillips et al. (1989)). At high temperatures, the term due to the free energy rather than the transport term controls the growth process.

During a growth rate experiment, the induction time for transcrystallization to appear can also be recorded. As shown in the previous section, this time carries the same informations on the energetics of the system as the nucleation rate. A plot of $\ln(1/t_i) + \Delta\phi/kT$ versus $1/T(\Delta Tf)^2$ should yield a linear curve whose slope is proportional to $\sigma\sigma_e\Delta\sigma$, from which $\Delta\sigma$ can be deduced. Such a curve is shown in Fig. 8.21. However, one would like to test the validity of Eq. (8.22) on a system where both the induction time and the nucleation rate can be measured at the same time. In their work, Ishida and Bussi (1990b) selected the bulk poly(ϵ-caprolactone) matrix as a test system because it also provides with an estimate of $\Delta\sigma'$ (Fig. 8.22). They noticed that the value of the induction time was much less sensitive to the melt history than the value of the nucleation rate. Their data shows that the plot of $\ln(1/t_i) + \Delta\phi/kT$ versus $1/T(\Delta Tf)^2$ and the plot of $\ln I + \Delta\phi/kT$ versus $1/T(\Delta Tf)^2$ have a very similar slope, which indicates that Eq. (8.22) is valid for the polymer tested. Thus the idea of interchangeability of induction time data with nucleation rate data for transcrystalline systems seems reasonable.

Chatterjee and Price (1975c) also collected $\Delta\sigma$ and $\Delta\sigma'$ data using the value of the surface nucleation rate. For their study they had to work with partially transcrystalline system in order to distinguish the individual spherulites at the substrate surface. Their results along with those of Ishida and Bussi (1990a,b) are presented in Tab. 8.2, using the characteristic A parameter as introduced in Sec. 8.2.2:

Polymer / Substrate	$A = \Delta\sigma' / \Delta\sigma$	Morphology
poly(butene-1) polystyrene (film)	0.5	Spherulitic
poly(butene-1) polypropylene (film)	0.6	Spherulitic
polyethylene polyethylene (fiber)	1.3	Transcrystalline
poly(ε-caprolactone) polyethylene (fiber)	2.0	Transcrystalline

It can be seen that advantage A is larger than 1 for truly transcrystalline systems. The difference in nucleating ability between heterogeneous crystallization in the melt and at the fiber surface is more striking when the induction time for each process is reported as a function of the crystallization temperature (Fig. 8.23). Such a diagram enables one to predict and control the morphology when it is coupled with transcrystalline growth rate data. If a temperature such as 52°C in Fig. 8.23 is selected, transcrystallization will appear after roughly 500 s. But for the same temperature, the induction time for massive nucleation to occur in the bulk matrix approaches infinity, which indicates that the nucleation rate becomes negligible. For this particular temperature, there is no competition from the matrix and transcrystals can grow unrestricted. Thus, it is possible to produce an entirely transcrystalline sample without having to use a high percentage of reinforcement (Fig. 8.24). The interest of such samples has been stressed earlier.

8.7 Conclusions / Outlook

Although transcrystallization has been observed for a long time in polymer films, it is a relatively new subject in the field of fiber reinforced semicrystalline thermoplastics composites. A look at the references in Sec. 8.8 confirms that most of the work which has been done in this area is less than five years old.

There are substantial evidences that transcrystallization improves the adhesion at the fiber/matrix interface and the mechanical properties of the interphase. Transcrystallization enhances interfacial adhesion by preventing the formation of a weak layer at the fiber surface. This weak layer is thought to consist of various impurities which are unable to crystallize. The transcrystalline growth front pushes these impurities away from the fiber surface, into the bulk matrix. The improvement in adhesion might also be an intrinsic property. It has been postulated that increased competition at the fiber surface during the nucleation step forces entanglements of the chains, which can act as crosslinks with the fiber. The transcrystals have also been found to posses a higher Young's modulus. However, this type of improvement in mechanical properties depends on the orientation of the transcrystals with respect to the strain direction.

These positive effects suggest that it might be advisable to induce transcrystallization in practical applications. Several methods can be suggested; coating of the fiber with a substance whose unit cell parameters match those of the polymer matrix, chemical treatment of the fiber surface to create favorable surface energy conditions, selection of a proper (i.e higher) crystallization temperature, mechanical treatment of the fiber to increase roughness and thus provide more potential nucleation sites, etc. Several questions merit further

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study; degree of crystallinity of the transcrystalline zone compared to that of the spherulitic bulk matrix, thickness of the transcrystalline lamellae (and effect of the crystallization temperature on this thickness) compared to that of the bulk spherulites, etc. More experimental data are also needed to evaluate the effect of the extent of the transcrystalline zone on the mechanical properties (i.e is there an optimum thickness ?).

Recent theoretical developments suggest that it might be possible to compare the nucleating ability of various polymer/substrate pairs on a quantitative basis. Lastly, the knowledge of the temperature dependency of the transcrystalline growth rate and the induction time enables one to control the extent of the transcrystalline zone to yield samples with known morphology.

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8.9 Acknowledgements

a)

Single nucleus   Series of nuclei forcing perpendicular growth

b)

50 μm
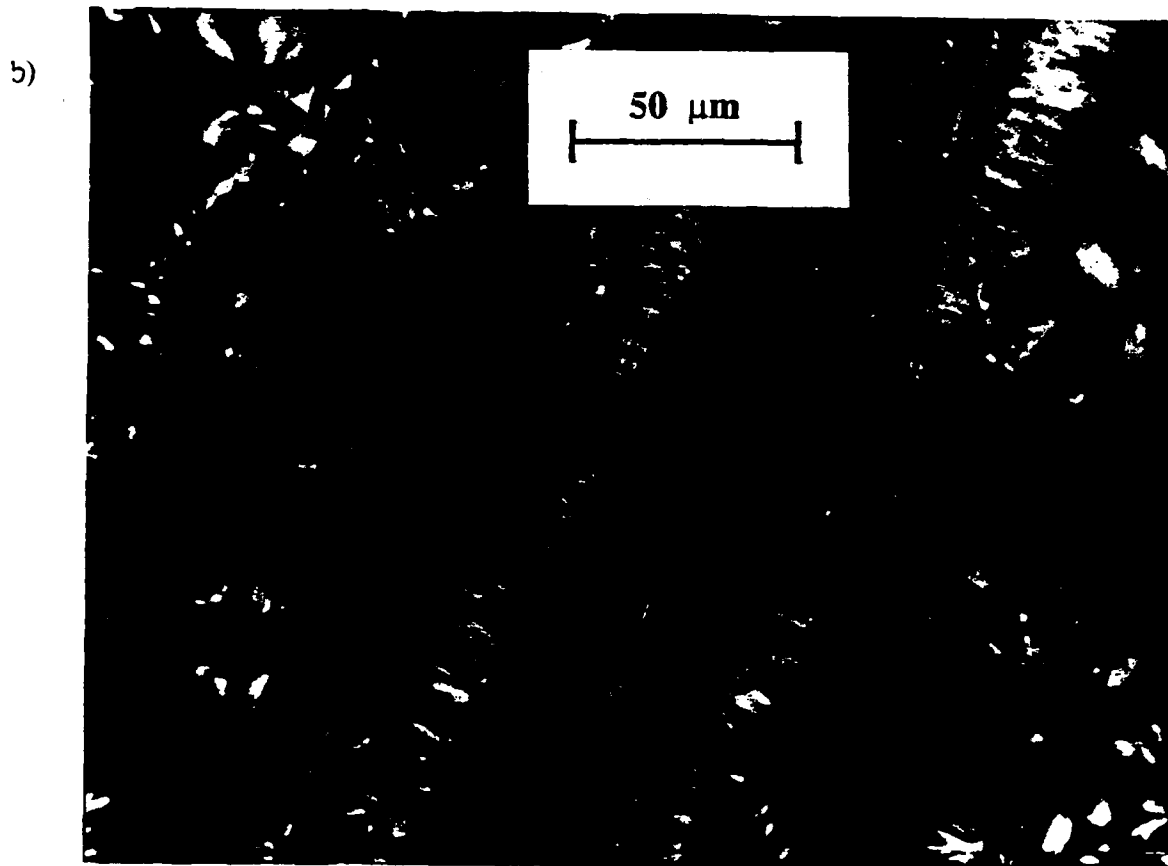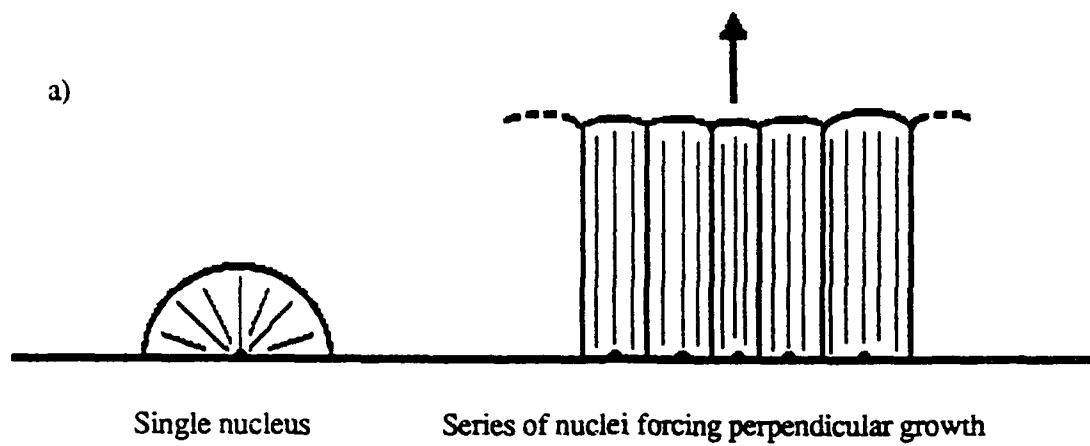
Figure 8.1 - a) Model for the formation of a transcrystalline zone: because of the large density of surface nuclei. growth can only proceed perpendicular to the substrate surface (after Sharples. 1966). b) Typical example of transcrystallinity in an ultra-high modulus polyethylene fiber reinforced polyethylene composite (T = 126.5 °C. after 15 min) (Ishida and Bussi. 1990a).

ΔG

ΔG*

critical nucleus

0

g*

Size g

embryo

supercritical

stable
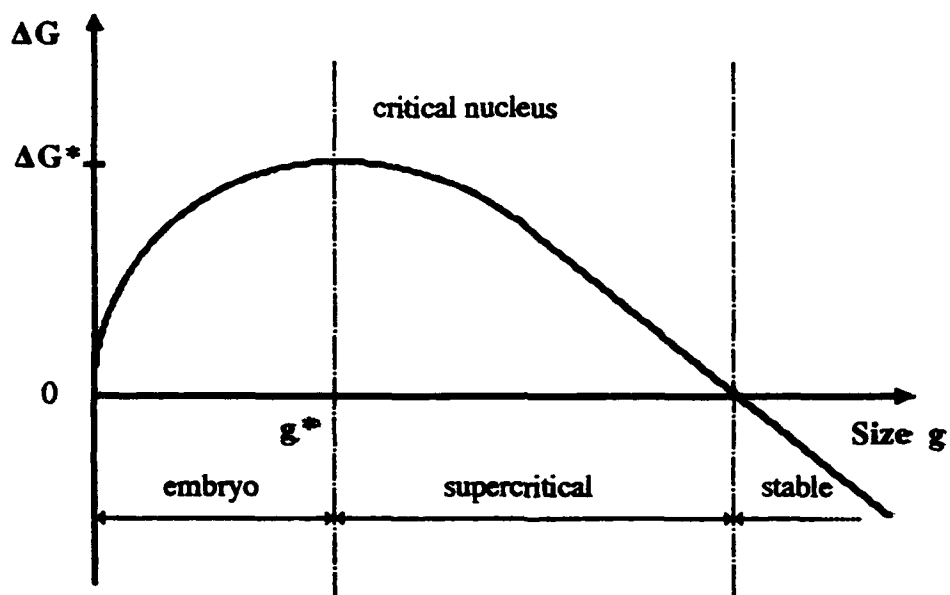
Figure 8.2 - Change in free enthalpy ΔG as a function of size g (after Wunderlich, 1976).
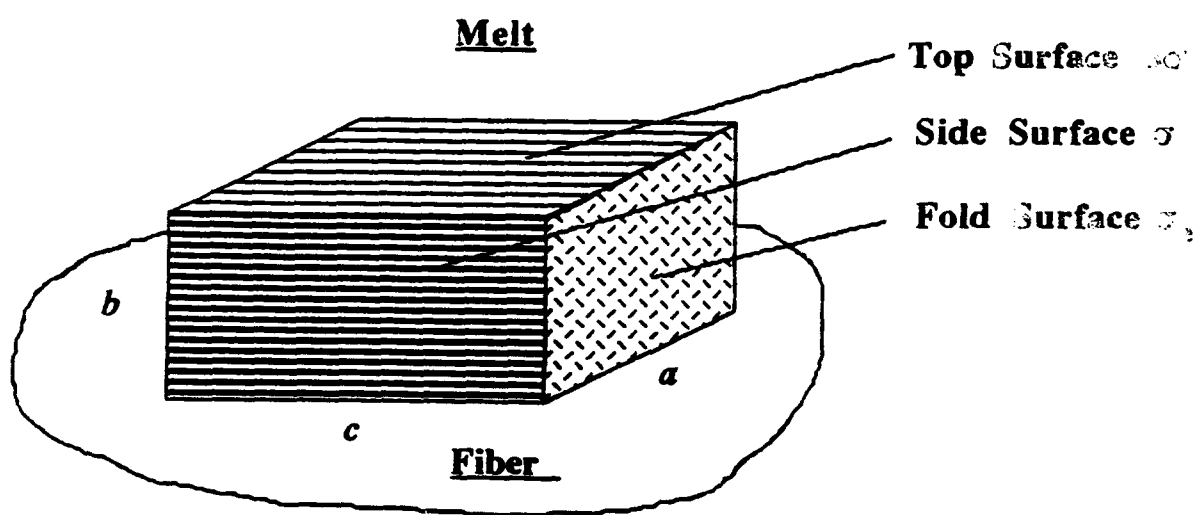
Figure 8.3 - Surface free energy parameters defining the heterogeneous nucleus.
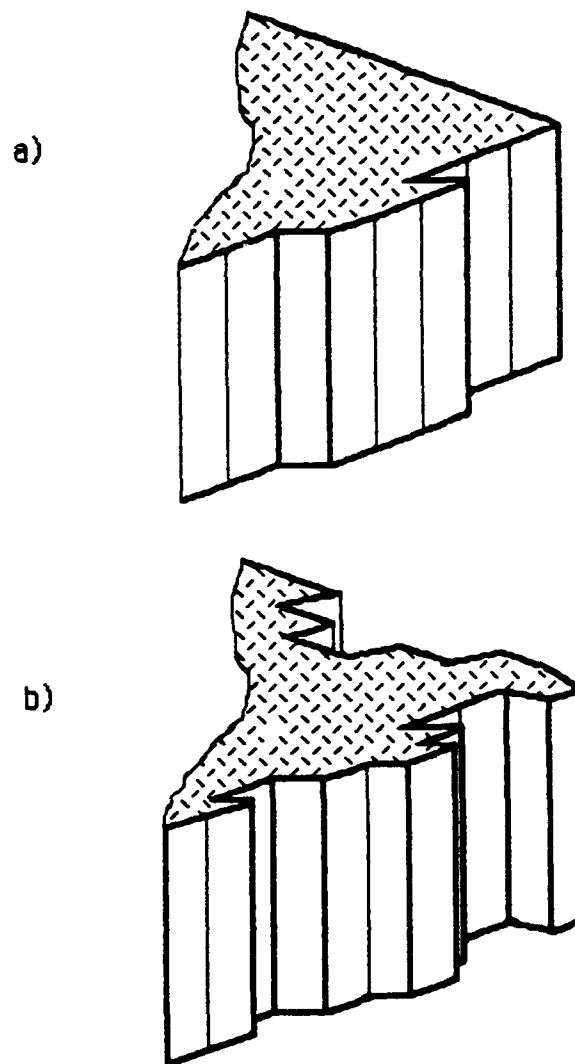
Figure 8.4 - Growth front morphology for Regime I and Regime II growth.

a) Regime I: Single nucleus forms on surface, rapid completion of a new layer.

b) Regime II: New surface nuclei appear before a layer is completed (after Hoffman et al., 1976).
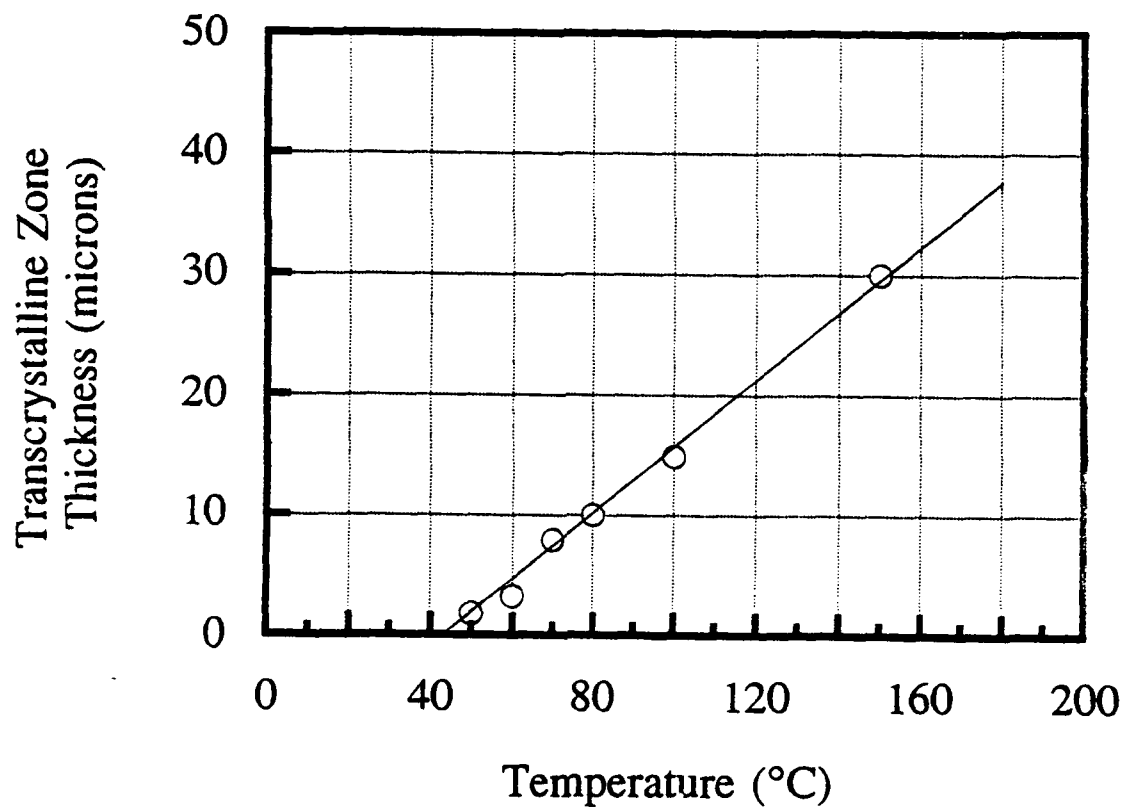
Figure 8.5 - Effect of the quenching temperature on the thickness of the transcrystalline zone (Polyamide film quenched in water from 240°C) (after Jenckel et al., 1952).
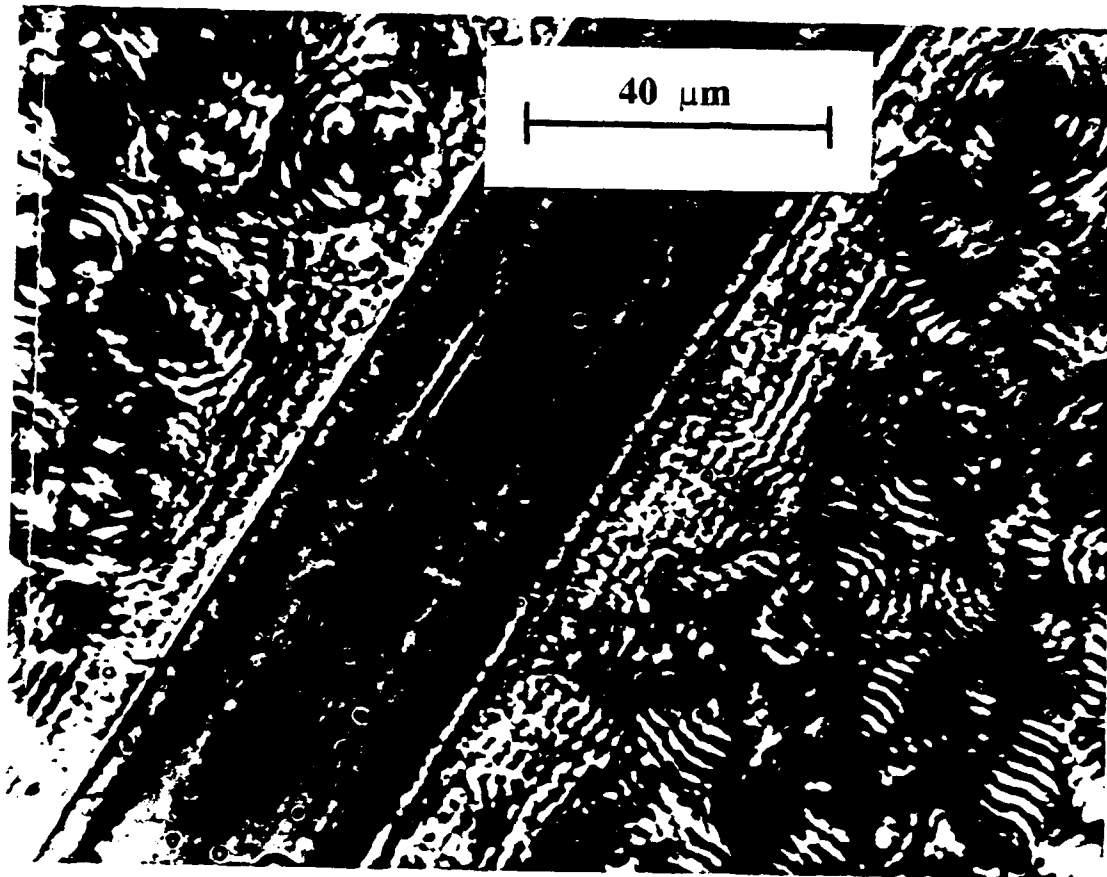
Figure 8.6 - Banded transcrystalline zone observed as a result of rapid cooling of a polyethylene/polyethylene composite film in air. Notice the parallel extinction lines near the fiber surface (Ishida and Bussi, 1990a).
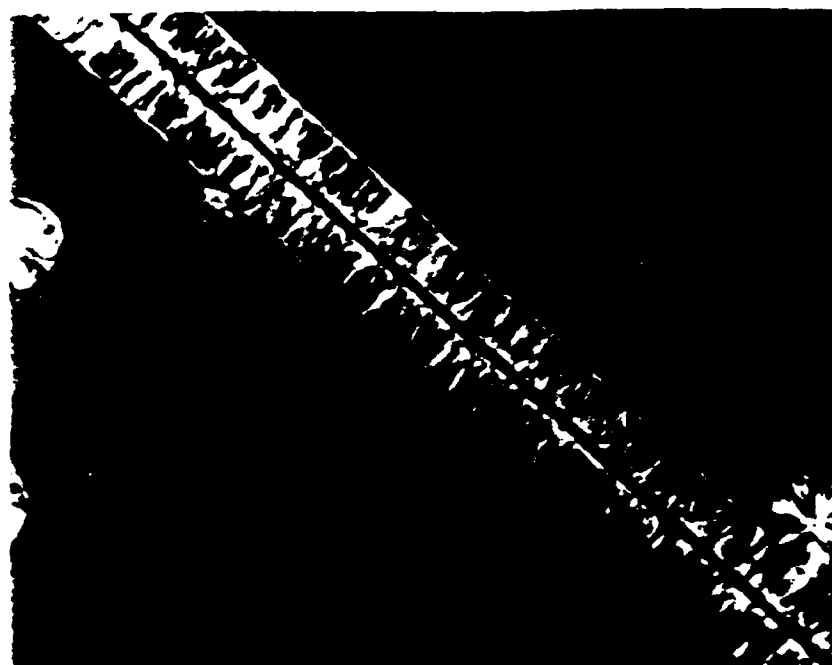
Figure 8.7 - Influence of the surface morphology of carbon fiber on the crystallization of polypropylene. a) Carbon fiber with small and disoriented graphite planes (type I fiber). b) Carbon fiber with large regular graphite planes (type II fiber) (Hobbs. 1971).
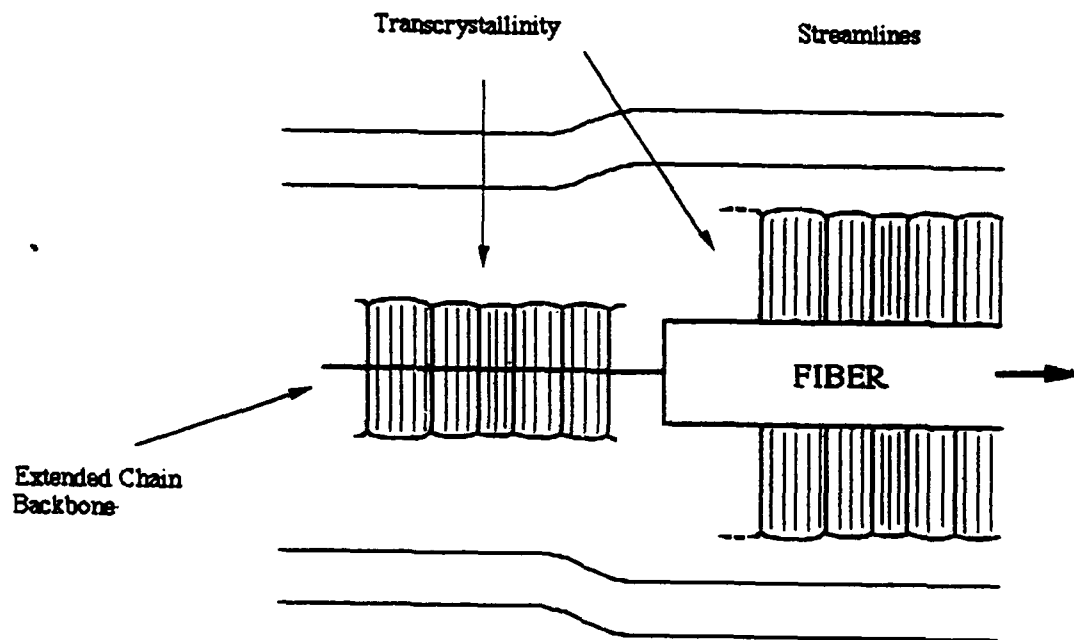
Figure 8.8 - Influence of flow pattern on surface crystallization. Transcrystallization is not only seen at the fiber/matrix interface, but also as a "tail" in the region where extensional flow has occurred (after Burton et al., 1984).
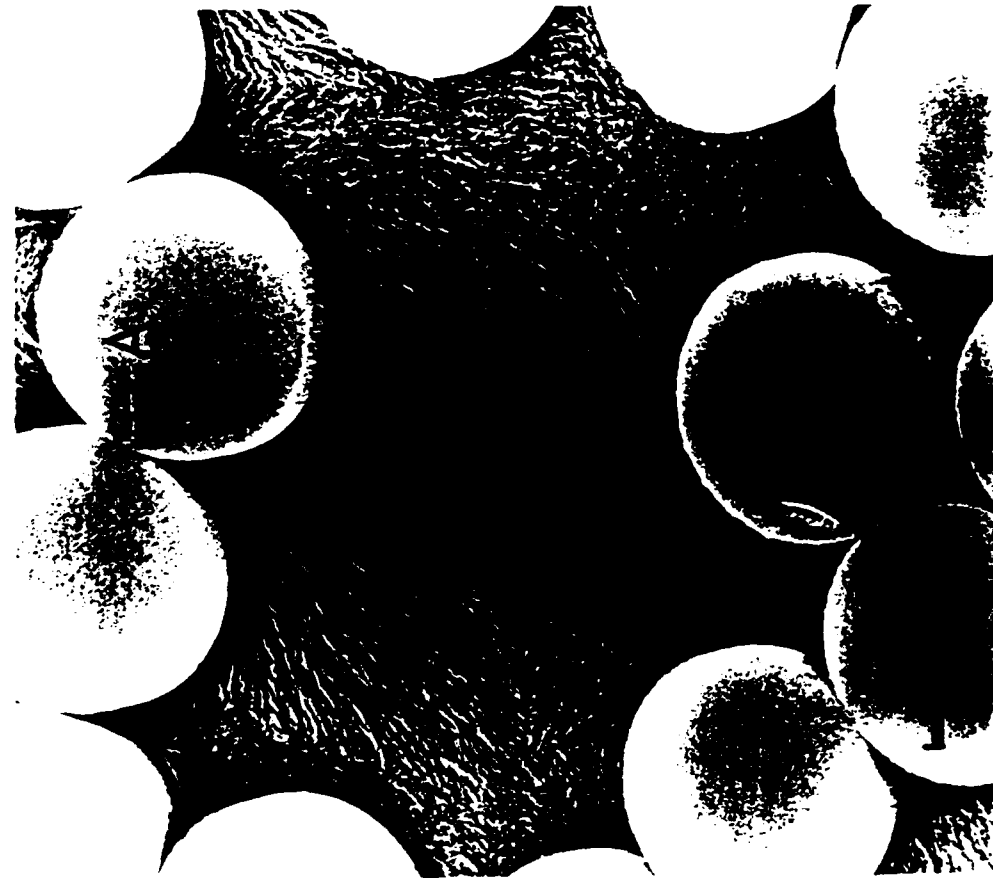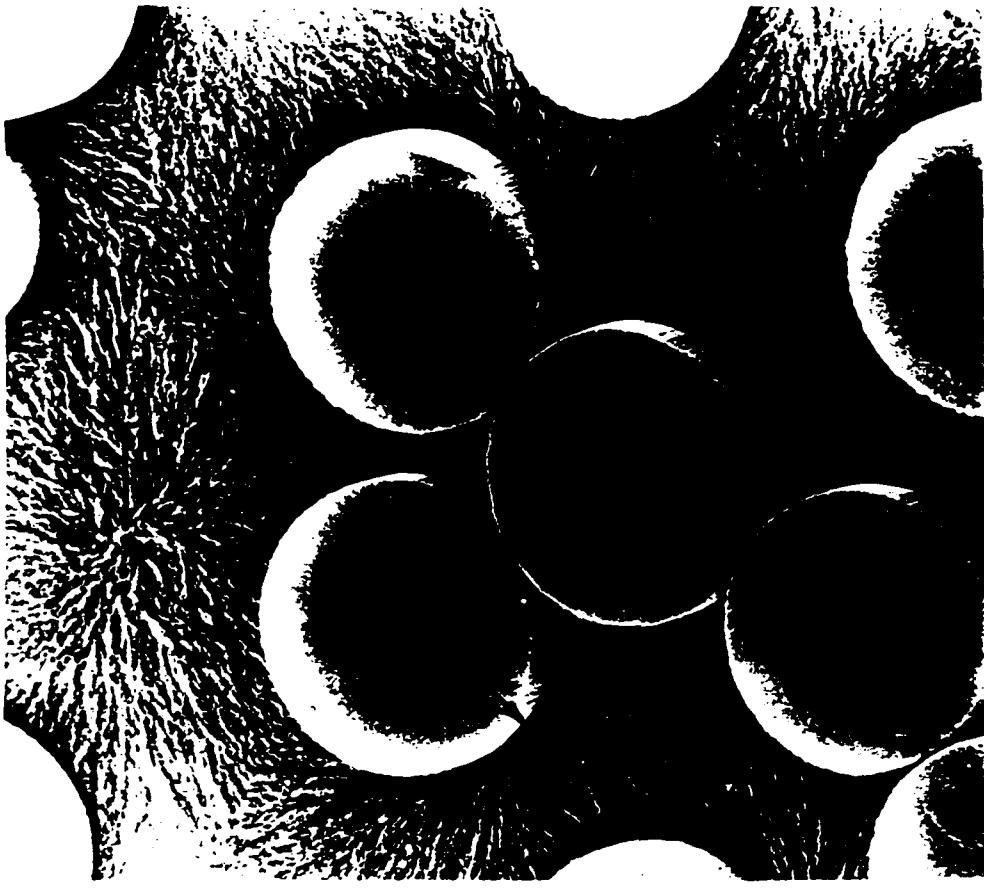
Figure 8.9 - SEM reveals that crystallization predominantly occurs at the fiber surface in carbon fiber/PEEK composites. Also notice that numerous spherulites are initiated between very close fibers (A), where, presumably, thermally induced stresses are larger (Peacok et al., 1986).
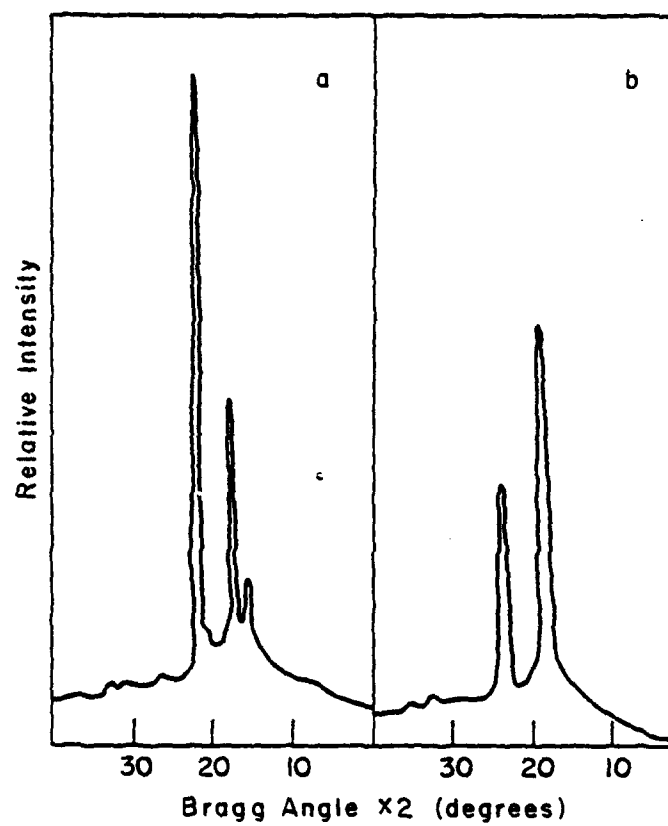
Figure 8.10 - Transcrystallization strongly influences the relative intensity in a reflection X-ray diffractogram. a) transcrystalline *trans*-1,4-polyisoprene fraction. b) spherulitic material (Lovering, 1970).
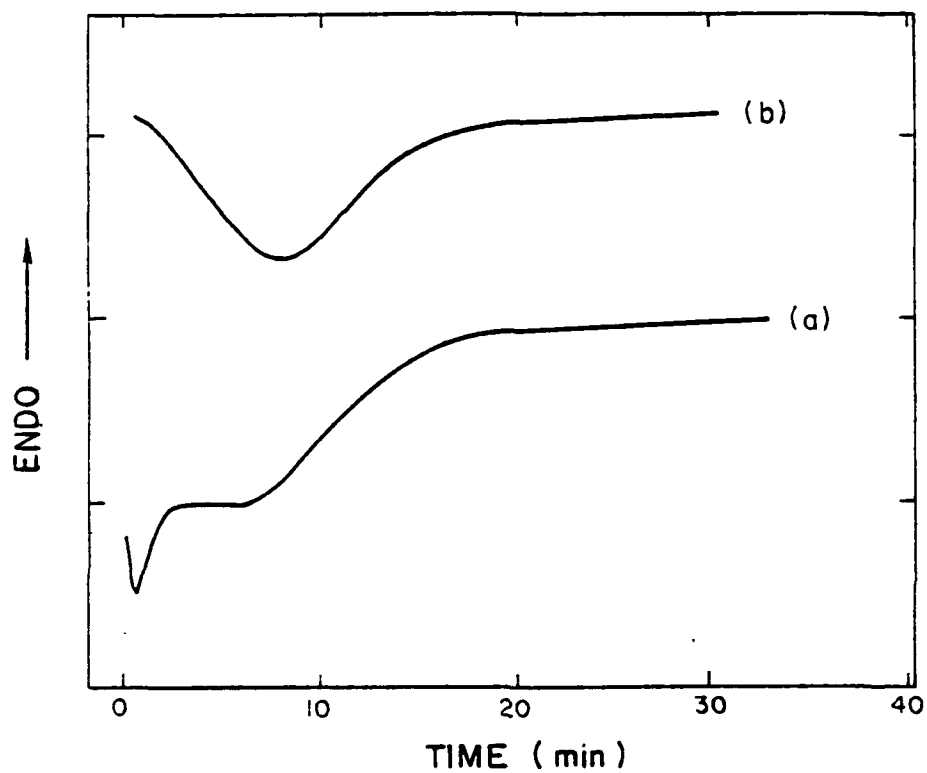
Figure 8.11 - DSC thermogram for the isothermal crystallization (124°C) of
a) polyethylene/polyethylene composite (50% wt fiber) and b) pure polyethylene matrix (He
and Porter, 1988).
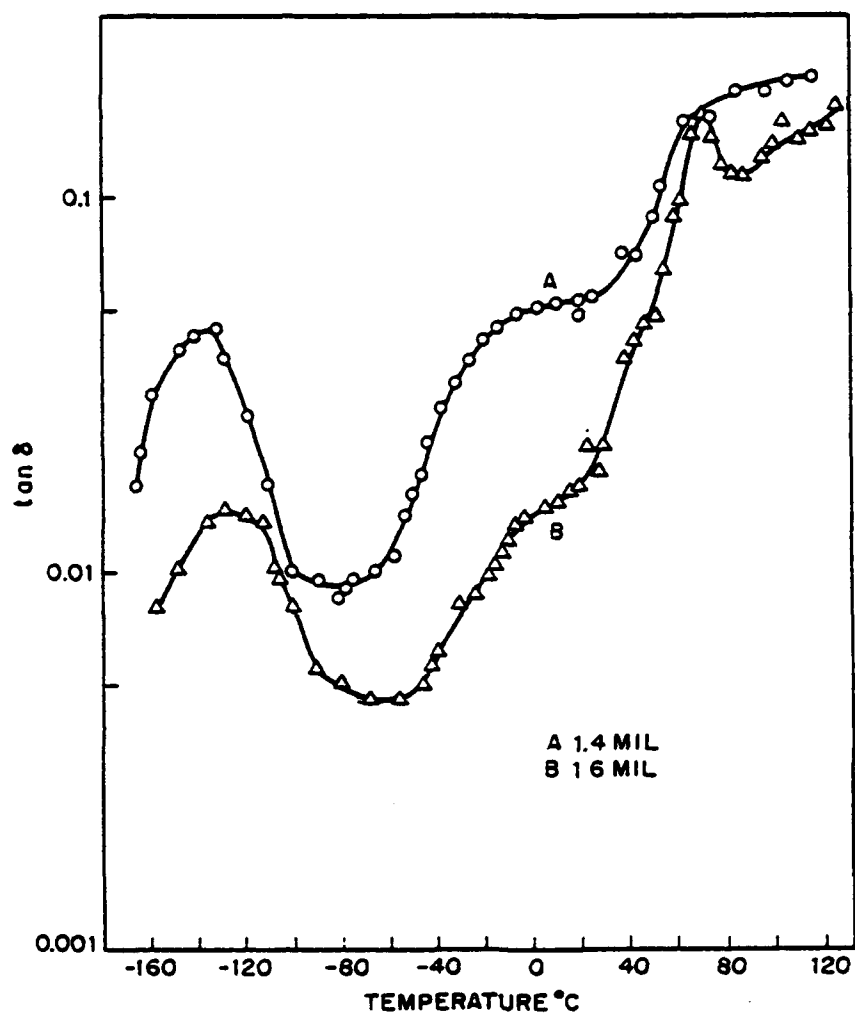
Figure 8.12 - DMS spectrum of a) transcrystalline polyethylene film and b) regular spherulitic film. Notice the higher loss factor, tan δ, for the transcrystalline film (Matsuoka et al., 1968).
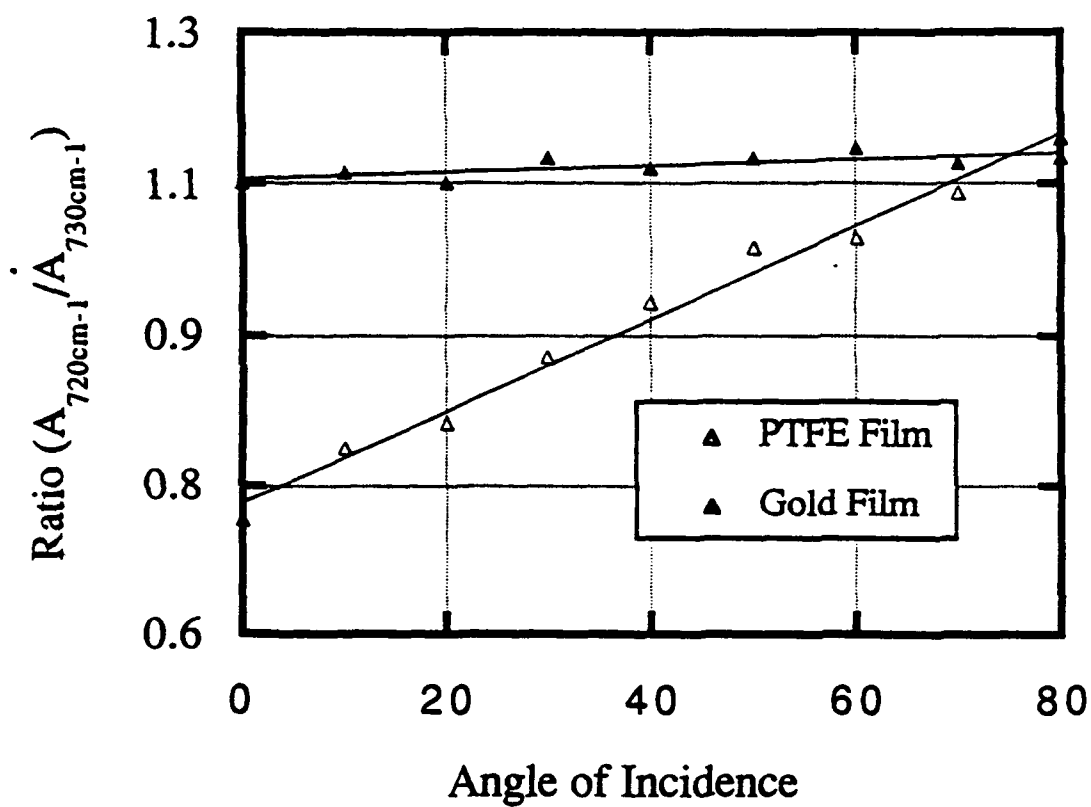
Figure 8.13 - ATR spectroscopy as a method of detection of surface orientation (polyethylene crystallized in contact with gold and polytetrafluoroethylene). The characteristic ratio, $R_{720/730}$, depends on the angle of incidence for the oriented structure (Luongo and Schonhorn, 1968).
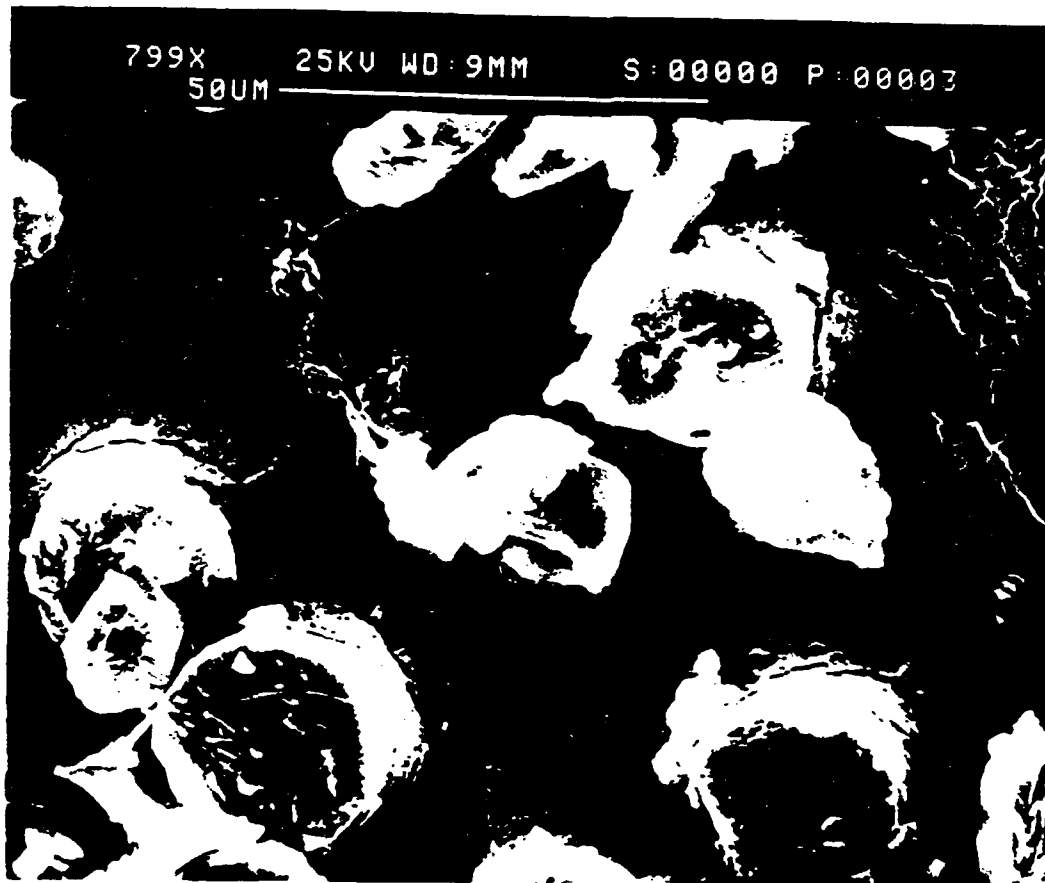
Figure 8.14 - In polyamide/glass fibers composites, failure occurs at the transcrystalline zone/bulk matrix interface rather than at the fiber /transcrystalline zone interface. This suggests increased adhesion at the fiber surface (Guigon et al.,1989).
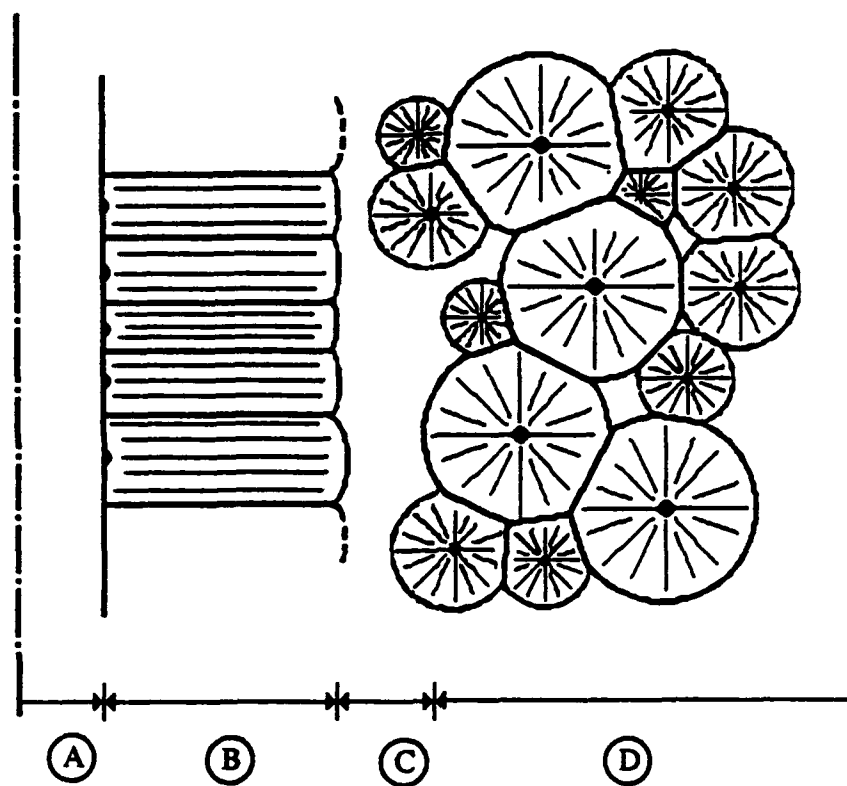
A: FIBER
B: TRANSCRYSTALLINE ZONE
C: INTERFACE TRANSCRYSTALLINE ZONE/BULK MATRIX
D: BULK MATRIX

Figure 8.15 - Schematic representation of a fiber reinforced semicrystalline thermoplastic system.
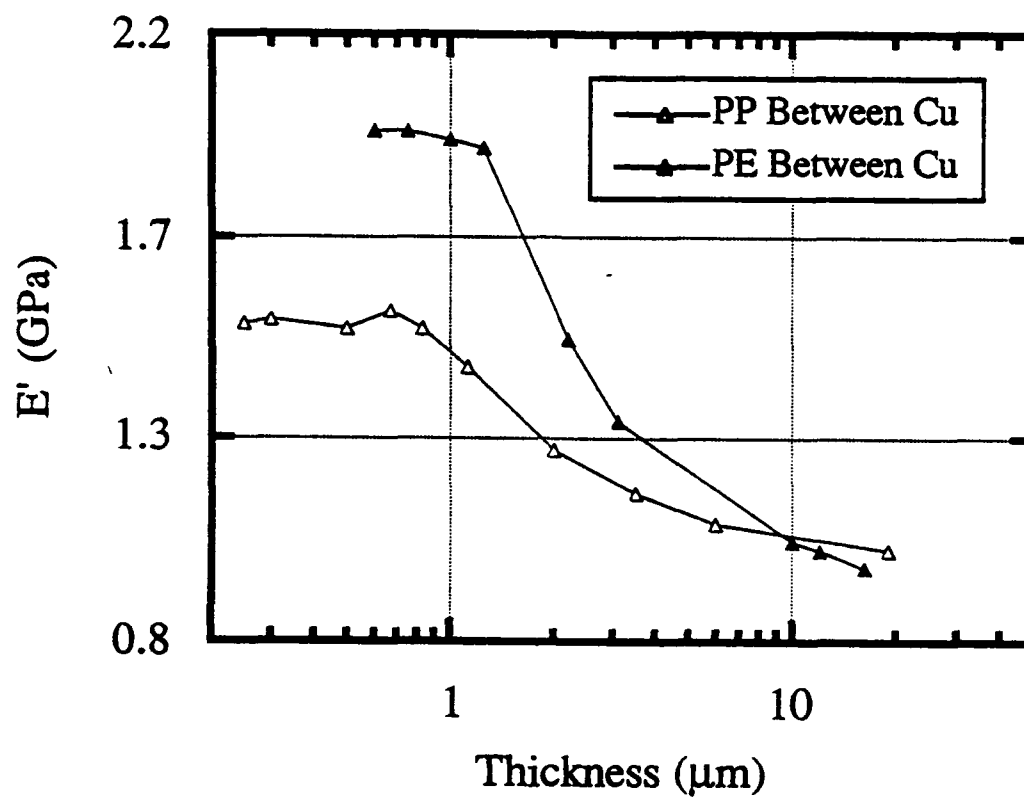
Figure 8.16 - Dependence of the real part of the Young's modulus, E', on the thickness of a polyolefin film. As the thickness decreases, the value of the modulus reaches a maximum, which corresponds to the value of the modulus for a purely transcrystalline film (Kwei et al., 1967).
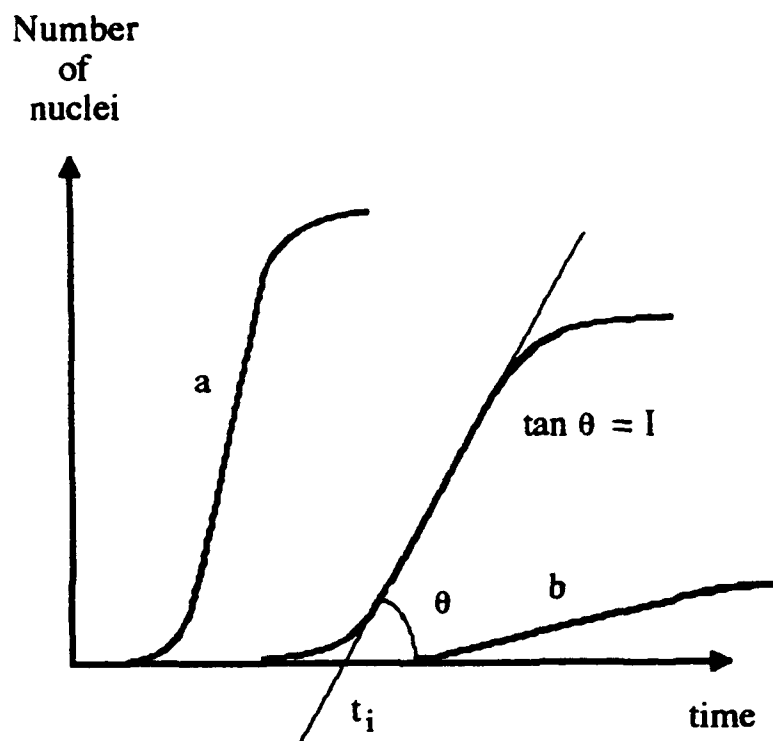
Figure 8.17 - Definition of the nucleation rate I and the induction time t_i.

a) Rapid nucleation, $I \to \infty$ and $t_i \to 0$, b) Slow nucleation, $I \to 0$ and $t_i \to \infty$.
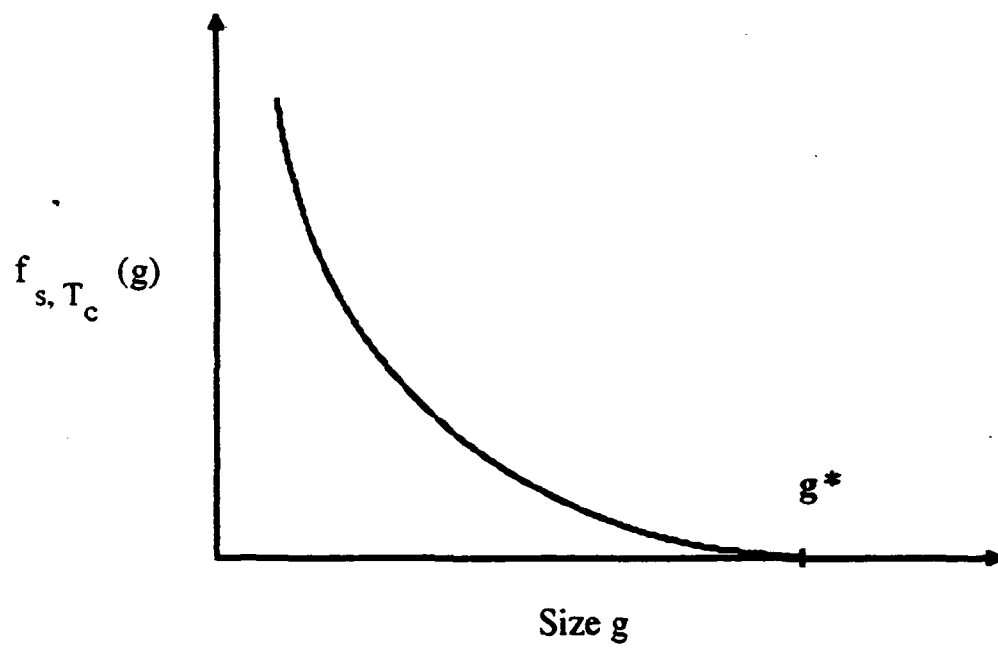
Figure 8.18 - Steady state distribution of subcritical nuclei as a function of size at a given temperature (after Wunderlich, 1976).
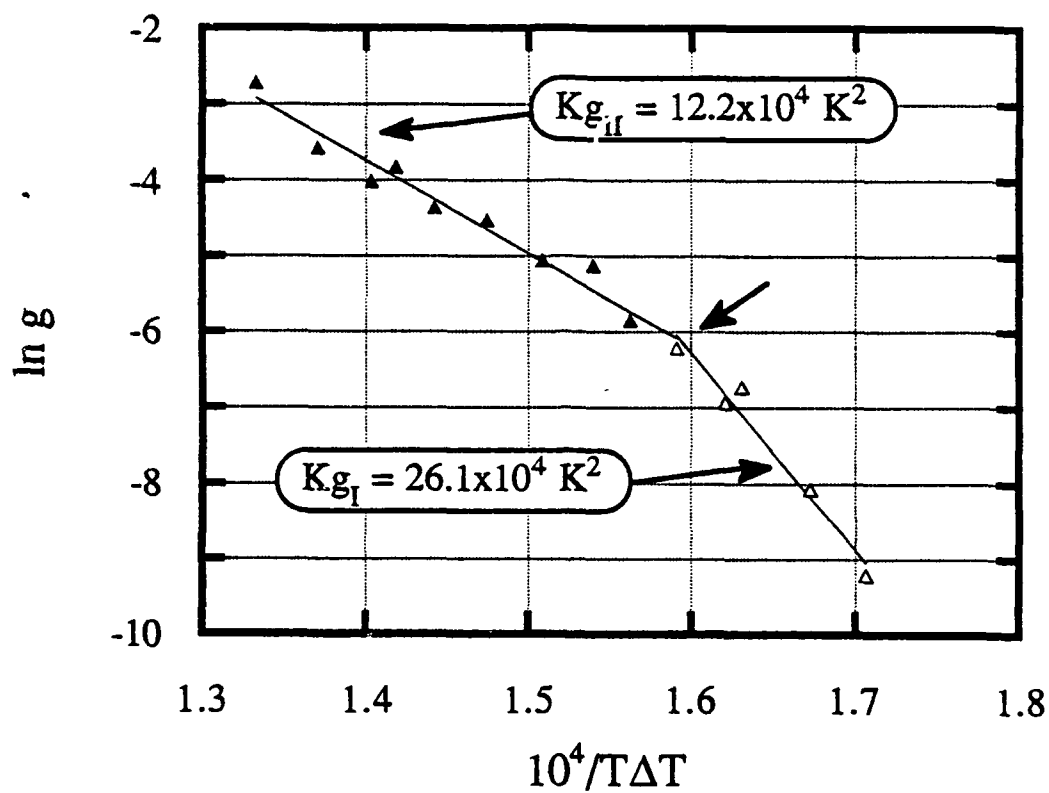
Figure 8.19 - Transcrystalline growth rate analysis for PE/PE composite. Plot of ln g versus 1/TΔT. The change in growth regime is indicated by the arrow (Ishida and Bussi, 1990a).
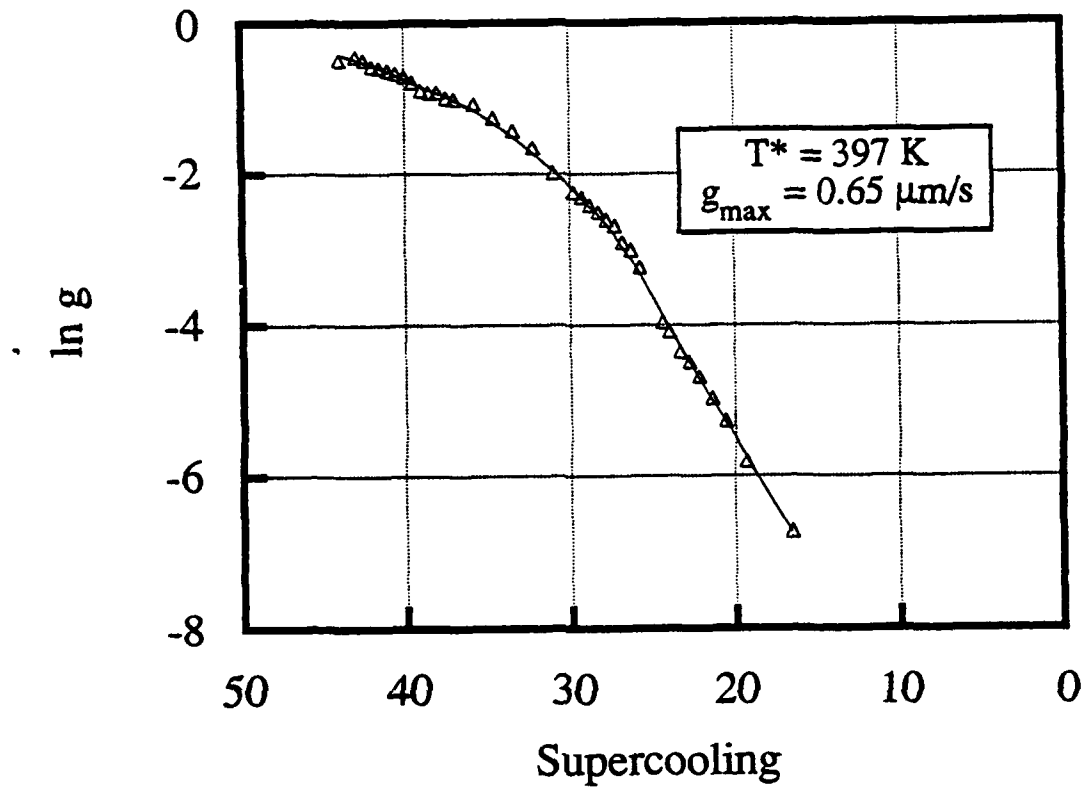
Figure 8.20 - Transcrystalline growth rate analysis for PCL/PE composite. As the supercooling increases, the transport term becomes predominant and the growth rate reaches a maximum value, g_{max} at the temperature T^* (Ishida and Bussi, 1990b).
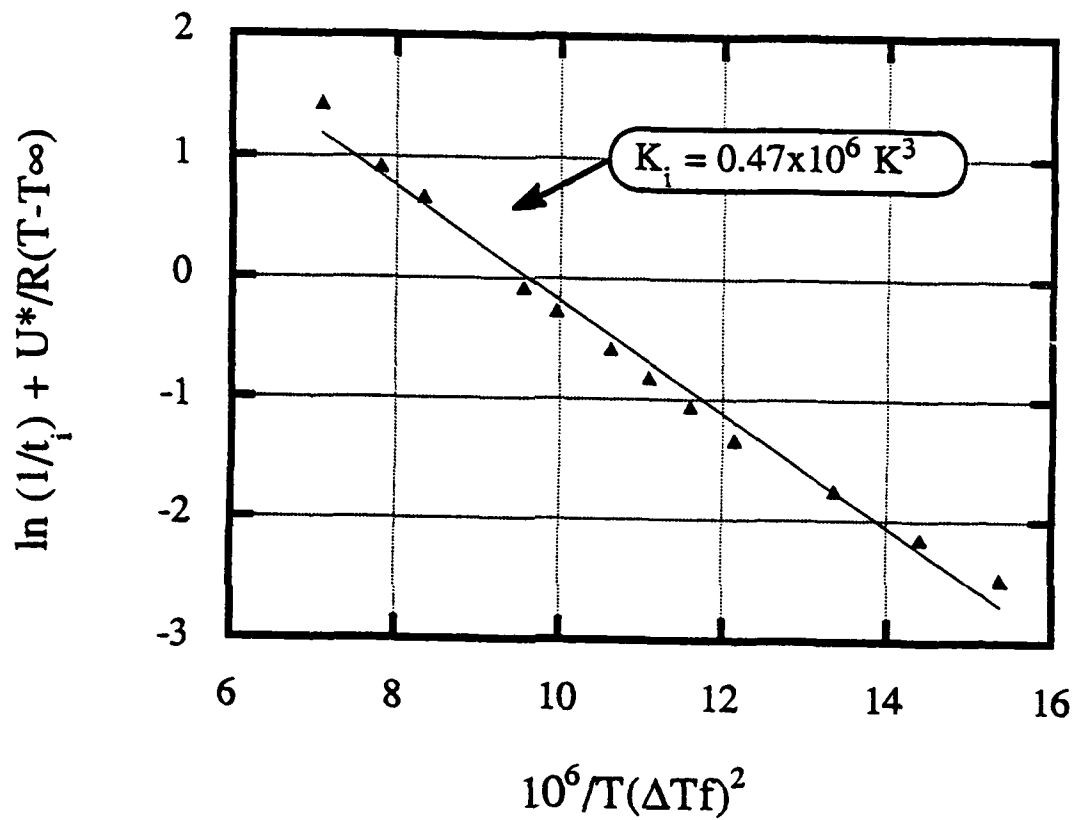
Figure 8.21 - Determination of the value of the free energy difference function, $\Delta\sigma$, from the temperature dependency of the induction time (Ishida and Bussi, 1990b).
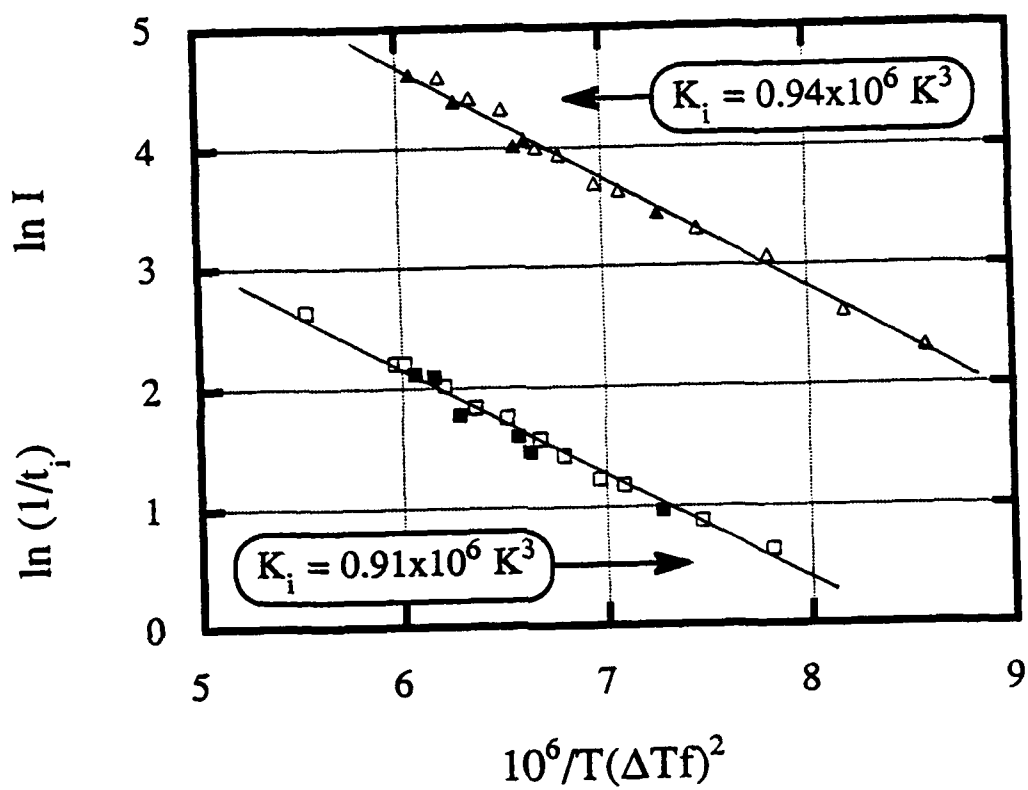
Figure 8.22 - Comparison of the induction time and the nucleation rate approach for the PCL melt. The similar slope of these two curves suggests that Eq. (8.22) is valid for the polymer considered (Ishida and Bussi, 1990b).
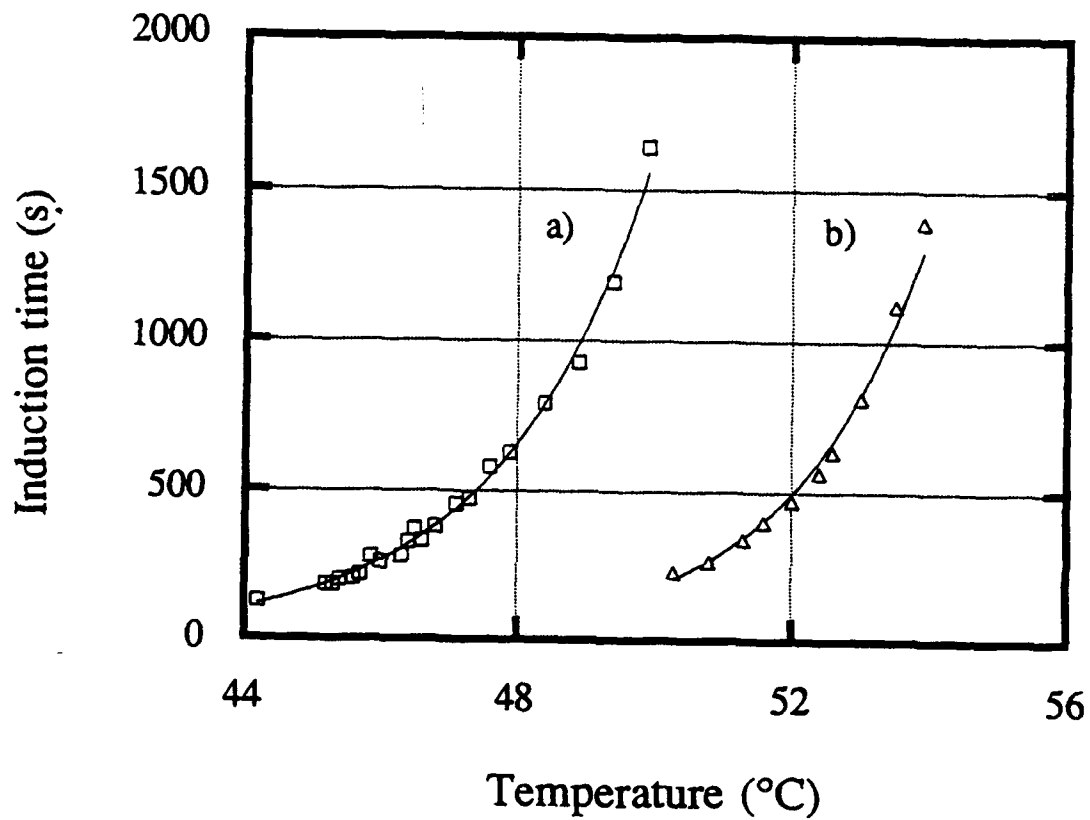
Figure 8.23 - Temperature dependency of the induction time for a) massive bulk nucleation and b) transcrystallization (PCL/PE composite). Notice the large difference for the temperature associated with each process, at a given induction time (Ishida and Bussi, 1990b).
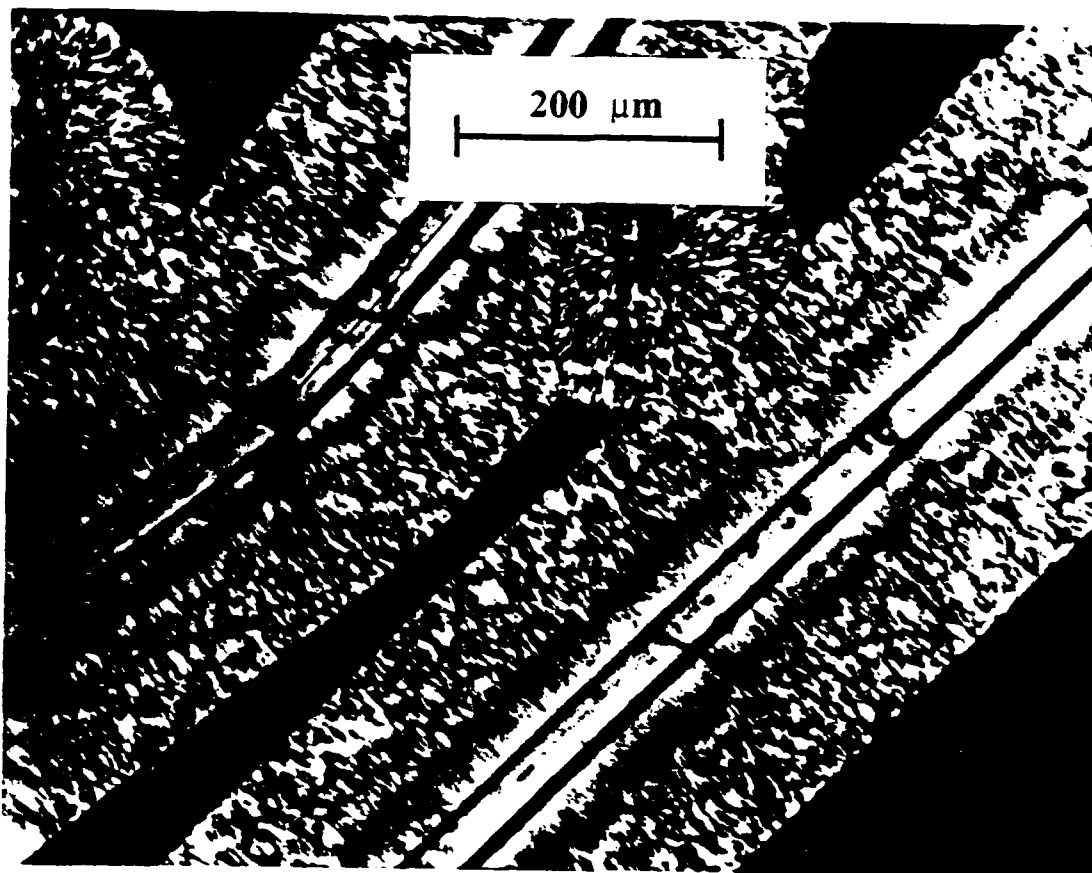
Figure 8.24 - Growth of a highly transcrystalline film with low percentage fiber (PCL/PE composite at 52 °C, after 20 h).